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Proceedings
September 10-13, 1989
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THIRD

INTERNATIONAL CONFERENCE

ON

NEW FRONTIERS FOR HAZARDOUS WASTE MANAGEMENT

Proceedings

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Sponsored by

Risk Reduction Engineering Laboratory
Office of Research and Development
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United Nations Environmental Programme
Paris, France

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FOREWORD

The managing of hazardous waste has proved itself to be of vast world concern. Because of this, the United States Environmental Protection Agency (USEPA) has developed a keen interest in working with environmental specialists from all nations. We view face-to-face conferences with our peers from many lands to be the most effective method of learning the problems and solutions so important to us all. The papers given at the sessions of this meeting will, we are certain, bring greater understanding of what we must accomplish to return this, our earth, to as close to its primal being as possible. -- At USEPA we feel if we, as world citizens, fail in this mission we will leave a reminder for future generations of our dereliction as they suffer the consequences. We must not fail and so we come to this international gathering to learn from the work being done in other lands and to share our own findings.

As one of your hosts at the Third International Conference on New Frontiers for Hazardous Waste Management USEPA's Risk Reduction Engineering Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving the problems posed by hazardous waste in the environment. Its products support the policies, programs, and regulations of USEPA, the permitting and other responsibilities of State and local governments, and the needs of both large and small businesses in handling their wastes responsibly and economically.

These Proceedings present the papers from this Third International Conference. USEPA, United Nations Environmental Programme, World Federation of Engineering Organizations, American Academy of Environmental Engineers, and NUS Corporation have cosponsored this conference in order to summarize important new technological developments and concepts with broad international application.

E. Timothy Oppelt
Director
Risk Reduction Engineering Laboratory

ABSTRACT

The Third International Conference on New Frontiers for Hazardous Waste Management was held at Pittsburgh, Pennsylvania, September 10-13, 1989. The purpose of this conference was to examine the state of technology for the disposal of hazardous waste. Emphasis was placed on the presentation of papers that summarized important new technological developments and concepts with broad international application.

Sessions were held in the areas of : (1) Thermal Treatment, (2) Physical/Chemical Treatment, (3) Biological Treatment, (4) Land Disposal, (5) Solidification/Stabilization, (6) Waste Minimization, and (7) Waste Management.

These Proceedings are a compilation of the speaker's papers. Where material for the entire work of a presenter was not available for primary publication, copies of the full paper may be obtained in the Conference lobby or later, by contacting NUS Corporation at their Pittsurgh address.

Due to the press of time and distance, manuscripts for five presentations were not included in these Proceedings. To obtain copies please enquire at the Conference registration desk or, following the conference, contact NUS Corporation at their Pittsburgh Address.

A topical index is located at the back of the book. We hope you find it useful.

This Conference was sponsored by United States Environmental Protection Agency, United Nations Environmental Programme, World Federation of Engineering Organizations, American Academy of Environmental Engineers, and NUS Corporation,

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EVALUATION OF TREATMENT TECHNOLOGIES FOR CONTAMINATED SOIL AND DEBRIS

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ABSTRACT

The performance of bench-scale treatment technologies on Superfund site soil samples was evaluated. The data were required to assist EPA in the study of alternatives for treating Superfund soils. Soils from three Superfund sites were selected for treatment evaluations. Three treatment technologies were evaluated: 1) chemical treatment (KPEG), 2) physical treatment (soil washing), and 3) low-temperature thermal desorption. An earlier study evaluated these three technologies on surrogate soils and also included incineration and stabilization. A brief comparison of results from actual Superfund soils with the surrogate soil will also be given. The following is a brief description of the three treatment technologies that will be discussed.

KPEG treatment of contaminated material involves mixing the waste with potassium hydroxide and polyethylene glycol, heating the waste/reagent mixture to 100° to 180°C for 1 to 5 hours, decanting excess reagent, washing the soil with water, and neutralizing and discharging the cleaned soil. The process has been successfully demonstrated for treatment of soil containing chlorinated biphenyls, dioxins, and furans. Decontamination is achieved through chemical dehalogenation of the aryl halide to form water-soluble reaction products.

Soil washing involves contacting the waste to be treated with a wash solution of chelate or anionic surfactant. The soil/reagent mixture is agitated for 15 to 30 minutes. Following agitation, the soil/reagent mixture is wet-sieved for particle size separation. Following chemical analysis, sieve fractions are either disposed of in a hazardous waste landfill or returned to the site as clean. Soil washing has been demonstrated to work for both inorganic and organic contaminants.

Thermal desorption involves heating organic-contaminated soils in a furnace to prescribed temperatures up to 550°F. As heating occurs, contaminants are released from the soil as gases that are purged from the system. The cleaned soils can then either be put back on site or disposed of in a Resource Conservation and Recovery Act (RCRA) landfill.

INTRODUCTION AND PURPOSE

In addition to addressing future land disposal of specific listed wastes, the RCRA land disposal restrictions also address the disposal of soil and debris from response actions under the Comprehensive Environmental Response Compensation and Liability Act (CERCLA). Sections 3004(d)(3) and (e)(3) of RCRA state that the soil/debris waste material resulting from a Superfund-financed response action or an enforcement authority response action implemented under Sections 104 and 106 of CERCLA, respectively, will be subject to the land ban. Because Superfund soil/debris waste often differs significantly from other types of hazardous waste, the EPA is developing specific RCRA Section 3004(m) standards or levels that apply to the treatment of these wastes. These standards will be developed through the evaluation of best demonstrated and available technologies (BDAT). In the future, Superfund wastes in compliance with these regulations may be deposited in land disposal units; wastes exceeding these levels will be banned from land disposal unless a variance is issued.

The data obtained in this study were required to assist EPA in the study of alternatives for treating Superfund soils. Under Phase I of this research program, which was conducted from April to November 1987, a surrogate soil containing a wide range of chemical contaminants typically occurring at Superfund sites was prepared for use in bench- or pilot-scale performance evaluations of five available treatment technologies: 1) physical treatment (soil washing), 2) chemical treatment (KPEG), 3) thermal desorption, 4) incineration, and 5) stabilization/solidification. Under Phase II of this research program, which was conducted from April to September 1988, contaminated soils from several Superfund sites were used to reevaluate (at bench scale) three of these treatment technologies: 1) chemical treatment utilizing a potassium polyethylene glycol reagent (KPEG), 2) physical treatment (soil washing), and 3) low-temperature thermal desorption. Stabilization/solidification was also conducted in Phase II; the stabilization results will be submitted in a separate report. Incineration was not evaluated in Phase II because of the expense involved in pilot-scale evaluation of incineration and the plethora of existing data on incineration of hazardous waste.

This report covers Phase II of EPA's research program for testing

Superfund soils and compares the Phase I and Phase II efforts. The bench-scale technology evaluations of KPEG, soil washing, and thermal desorption were essentially the same in Phases I and II. The use of actual contaminated soils in Phase II, however, produced different removal efficiencies for many of the contaminants than was observed during the Phase I investigations on surrogate soils.

APPROACH

Soil Characteristics

Soils from three Superfund sites were selected for these tests: Syncon Resins, Berlin-Farro, and Old Mill. Soils from Berlin-Farro and Syncon Resins were used for the KPEG and soil-washing processes, and soils from Berlin-Farro and Old Mill were used for the low-temperature desorption process. Table 1 gives the grain size characteristics for the three soils that were used.

Chemical Treatment--KPEG

During 1978, a new chemical reagent was synthesized and effectively used to dechlorinate PCB oils at the Franklin Research Center. Since that time, a series of reagents have been prepared from potassium hydroxide and polyethylene glycolates (KPEG) to degrade the polychlorinated biphenyls (PCB's), polychlorinated dibenzodioxins (PCDD's), and polychlorinated dibenzofurans (PCDF's) contained in soils and in other matrices such as waste herbicides and waste oils.

A typical KPEG process for treating contaminated soil involves mixing the soil with potassium hydroxide and polyethylene glycol (approximate molecular weight of 400), heating the soil/reagent mixture to 100° to 180°C, allowing the reaction to proceed for 1 to 5 hours, decanting the excess reagent, washing the soil two or three times with water, and discharging the clean soil. Figure 1 represents the bench-scale reaction vessel used in this study.

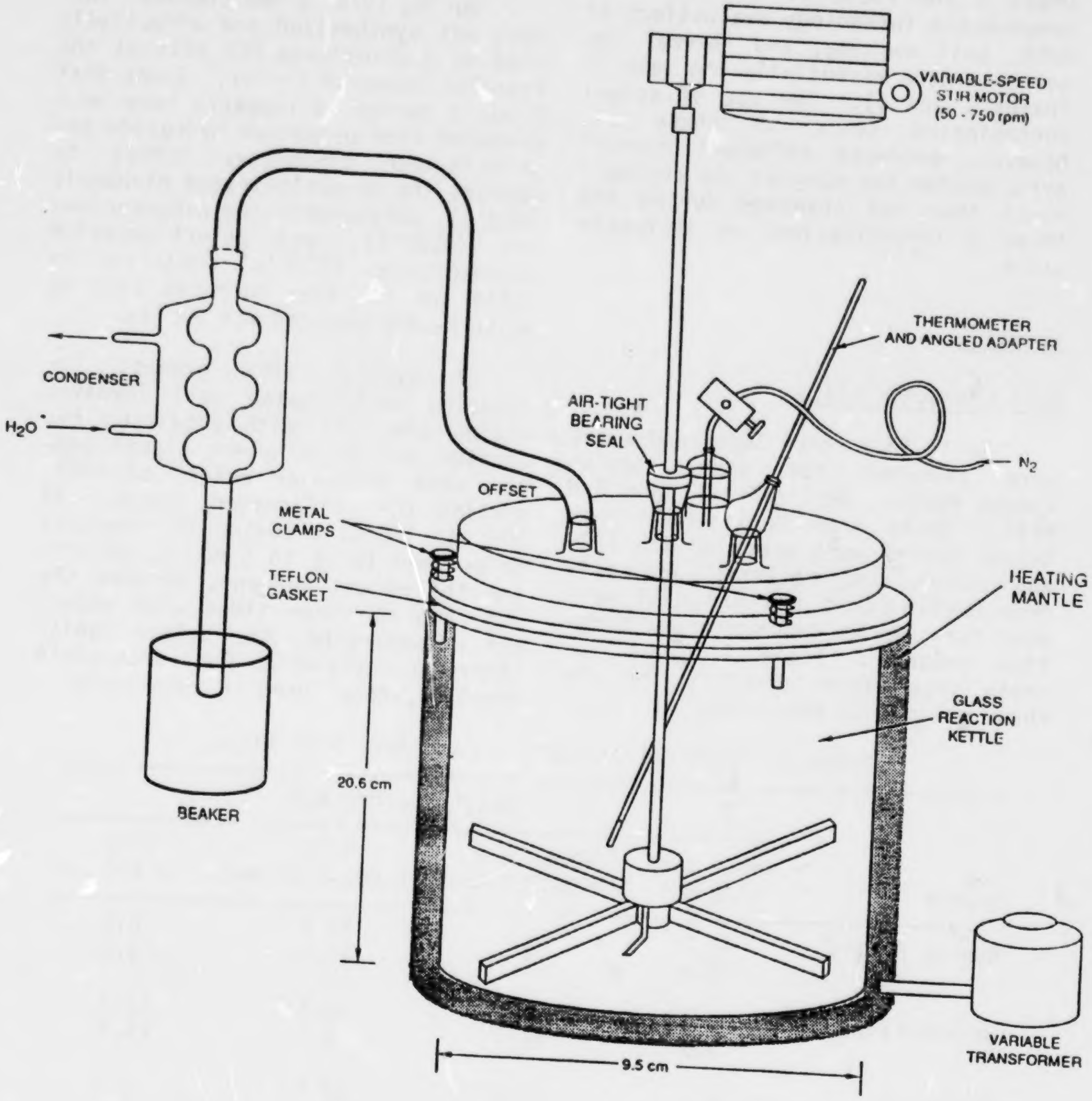
Table 1. Physical analysis - candidate test soils.

	Weight percentage			
Source	Coarse sand (>0.5 mm)	Fine sand (0.05-0.5 mm)	Silt (0.002-0.05 mm)	Clay (<0.002 mm)
Syncon Resins[a]	47.8	29.1	15.1	8.0
	29.8	47.0	15.0	8.2
Berlin-Farro[b]	4.2	35.2	33.4	27.2
	3.3	36.1	34.1	26.5
Old Mill[c]	28.2	40.3	22.6	8.9
	37.2	35.6	19.6	7.6

[a] The soil is primarily alluvial sand, silt, clays, and detritus (landfill soil).

[b] The soil is glacial till.

[c] The soil is a glacial silty clay that also has sand, gravel, and boulders.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GLASS REACTION KETTLE
BEAKER
20.6 cm
9.5 cm
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Figure 1. KPEG reaction vessel.

The reaction of potassium hydroxide with polyethylene glycol forms an alkoxide, which in turn reacts initially with one of the chlorine atoms on the aryl ring to produce an ether and potassium chloride salt. In some KPEG reagent formulations, dimethyl sulfoxide (DMSO) is added as a cosolvent to enhance reaction rate kinetics by improving rates of extraction of aryl halide wastes into the alkoxide phase.

The important feature offered by the polyethylene glycol-mediated dehalogenation reaction is a controlled process that occurs at relatively low temperatures (70° to 180°C). In contrast, more conventional dehalogenation processes using only solid caustic generally require substantially higher temperatures, and they are often violent (or even uncontrolled) processes.

Physical Treatment--Soil Washing

Soil washing is a physical treatment process in which soil particles are washed with an aqueous solution to separate the fine soil fraction (<2 mm) from the coarse fraction (>2 mm). The steps involved in soil washing are excavation of the contaminated soil, breakup of the soil agglomerates, separation of fine particles from coarse particles by physical cleaning and scrubbing with washing fluids, and treatment of the fines and spent wash solution. After the soil-washing process, the clean coarse fraction (>2 mm) can usually be deposited back on site without further treatment, which reduces the volume of the original contaminated soil. Contaminated fine particles can then be stabilized, incinerated, or subjected to chemical treatment. If additives are used in the tap water, recovery and reuse of the washing fluid are essential for an economical soil-washing treatment process.

Successful soil washing of contaminated soils is based on the following assumptions:

1) Fine particles (silt, clay, and humic material) adsorb a significant fraction of the contaminants in the soil.

2) The contaminated fine particles attach to coarse grains of the soil by electrostatic, chemical, hydrodynamic, and Van der Waals forces.

3) Physical washing of the sand/gravel/rock fraction effectively removes the fine sand, silt, clay, and colloidal-sized materials from the coarse material.

4) The removal of fine particles results in the removal of a significant portion of the contaminants that exist in that fraction.

Most of the soil-washing experiments conducted to date have shown that metals can be effectively removed from the >2-mm fraction by use of plain water or addition of a chelate solution. Organic contaminant removal has been enhanced by the use of surfactant solutions. If the contaminants are chemically bound to the soil particles, however, surfactants may not be able to remove them from the particles and mobilize them in the water (Dietz et al. 1986). Nevertheless, washing of soils containing hydrophobic organics has met with limited success.

The physical nature of the soils is also an important consideration in an evaluation of soil washing as a possible treatment technology. Generally, soils high in clay and humic content are difficult to treat because of their characteristically high cation exchange capacity and high specific surface area. These experiments entailed the use of three aqueous wash solutions:

1) Tap water for removing water-soluble compounds.

2) Chelate wash for removing metallic compounds. A solution was prepared containing a 3:1 molar ratio of ethylenediaminetetraacetic acid (EDTA) to total hazardous metals present in the soil.

3) Surfactant wash for removing organic compounds. A 0.5 percent (by weight) solution was prepared of industrial formula Tide (manufactured by Procter & Gamble).

Low-Temperature Thermal Desorption

Low-temperature thermal desorption is based on vapor pressure for removal of organic compounds. The thermal desorption process takes advantage of thermal driving forces to remove organic contamination while avoiding typical incineration processing conditions that are expensive or have negative public perception. Because thermal desorption is conducted at lower operating temperatures, it offers significant fuel savings over high-temperature incineration. The heat required for thermal desorption can be provided by indirect heating of the soils as opposed to direct-fired heating of solids in an incineration process. This greatly reduces the quantity of off-gases that must be cleaned prior to discharge. This design aspect not only reduces the cost of subsequent air pollution control, but also facilitates the design of a closed system with no visible plume. Thus, treatment of contaminated soils by thermal desorption can be more cost-effective on low-level organically contaminated soils and may be more readily accepted by the public.

The experimental approach was thermal treatment in static trays in an electric oven for specified periods of time. The removal of organic constituents was measured after treatment at two different test temperatures, 350° and 550°F, for 30 minutes. The effectiveness of treatment was measured by analysis of the soil before and after thermal desorption. Figure 2 is a schematic of the thermal desorber used in this study.

PROBLEMS ENCOUNTERED

Several problems were associated with the semivolatile analyses, and these data should be used with caution. The hold times were exceeded for analysis of the semivolatile organic extracts. Furthermore, the detection limit for many of the samples was in excess of what was necessary to make valuable conclusions concerning the treatment technologies' effectiveness. Finally, for pyrene, the only target compound subject to QA/QC analyses, the QC limits for accuracy and precision were exceeded.

RESULTS

Chemical Treatment--KPEG

The metals results indicate that none of the metals was removed by KPEG. KPEG is not designed to remove

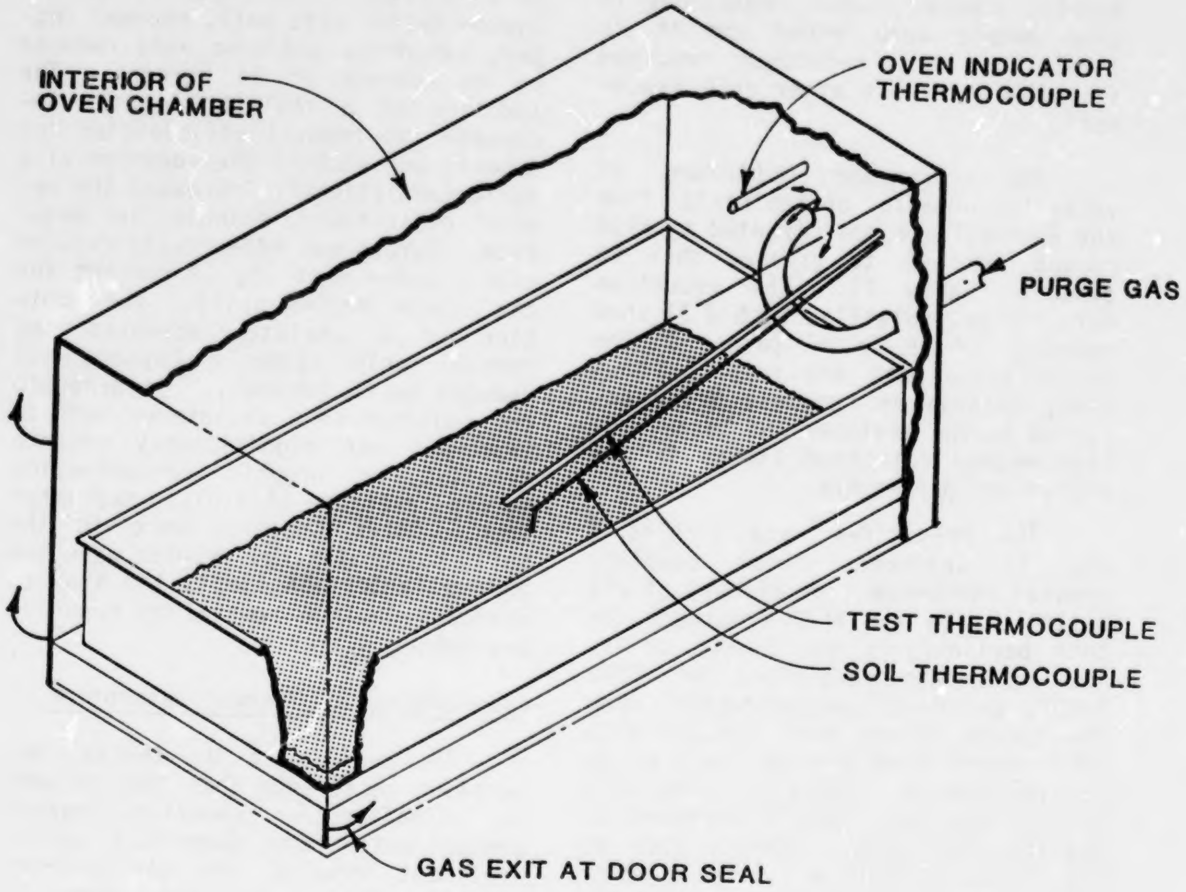
INTERIOR OF OVEN CHAMBER
OVEN INDICATOR THERMOCOUPLE
PURGE GAS
TEST THERMOCOUPLE
SOIL THERMOCOUPLE
GAS EXIT AT DOOR SEAL

Figure 2. Schematic of interior of static tray test oven with the tray inserted.

metals; however, small reductions in some metals were noted and it is likely that these reductions resulted from the acid wash after KPEG treatment.

The percentage reductions of volatile organic contaminants from the Berlin-Farro soil treated by KPEG ranged from 28 to greater than 93 percent (Table 2). The reduction data for semivolatiles (Table 3) show removals of 59 to 97 percent. The semivolatile data are suspect, however, because an extended delay occurred in the analyses and because of high method detection limits in the analytical parameters.

The pesticides data (Tables 4 and 5) indicate almost complete removal (98 percent or higher) of all pesticides by the KPEG treatment for both Berlin-Farro and Syncon soils. The percentage reductions in TCDF, PeCDF, and HxCDF concentrations from the Syncon Resins soil treated with KPEG ranged from greater than 57 to greater than 94 (Table 6). The KPEG process was specifically designed to degrade chlorinated organics such as PCB, PCDD, and PCDF and other contaminants (e.g., pesticides and herbicides). The substantial reduction in pesticides and some chlorinated dibenzofurans obtained during this study further supports the effectiveness of KPEG in removing these compounds from contaminated soils.

Physical Treatment--Soil Washing

The results from the evaluation of soil washing show that generally, most metals were effectively removed from the coarse fraction (greater than 2 mm in diameter) of the contaminated soils. Table 7 shows that water alone removed arsenic and lead in an average of 92 percent from the Syncon Resins site soil, whereas copper, vanadium, and zinc were reduced by an average of 64 percent. The addition of a chelate slightly increased the removal efficiencies for arsenic and nickel; the addition of a surfactant slightly increased the removal of antimony, arsenic, and vanadium. Pyrene was effectively reduced with a water wash (by 72 percent for the Syncon Resins soil). The addition of a chelate increased the removal only slightly (pyrene was reduced by 80 percent). In general, the addition of a chelate or surfactant did not significantly enhance metallic or organic contamination removal over use of a plain tap water wash. Other organics were in the soil, but analytical results were too poor or detection limits too high to indicate whether removal of organics was taking place.

Low-Temperature Thermal Desorption

The results of the thermal desorption tests show that this process is effective in removing organic contaminants from Superfund soils. Treatment results for Berlin-Farro and Old Mill soils are given in Tables 8 and 9, respectively. Volatiles ranged from 70 to 96 percent removal at 350°F and from 63 to 99 percent removal at 550°F for both soils. Semivolatiles ranged from 55 to 95 percent removal at 550°F for both soils. In the opinion of the authors, the lower ranges, such as 72 and 70 percent removal for toluene and xylenes, respectively, at Old Mill would be higher if it were not for poor analytical results because 94 and 96 percent removals were respectively obtained for these same two compounds at Berlin-Farro. Furthermore, Berlin-Farro had a higher

Table 2. Results of KPEG treatment of Berlin-Farro soils--volatile organic compounds.[a]

Parameter	Untreated soil, ppb	Treated soil, ppb	Percent reduction
Acetone	1200.0	633[b]	47.3
Trichloroethene	109.5[c]	<33.0	>69.9
Tetrachloroethene	500.0[c]	<33.0	>93.4
Toluene	580.0[c]	215[b]	62.9
Xylenes (total)	225.0[c]	161	28.4

[a] Results presented are averages of quadruplicate runs.

[b] Detected in blank.

[c] Estimated value.

Table 3. Results of KPEG treatment of Berlin-Farro soil--semivolatile organic compounds[a]

Parameter	Untreated soil, ppb	Treated soil, ppb	Percent reduction
Hexachlorocyclopentadiene	38,667	<4800	>87.6
Hexachlorobenzene	88,667	<2600	>97.1
Pentachlorobenzene	8,800[b]	<3565	>59.5

[a] Results presented are averages of quadruplicate runs.

[b] Estimated value.

Table 4. Results of KPEG treatment of Berlin-Farro soils--pesticides.[a]

Parameter	Untreated soil, ppb	Treated soil, ppb	Percent reduction
2,4-D	7163	169	97.6
Heptachlor epoxide	16.1	0.113	99.3

[a] Results presented are averages of quadruplicate runs.

Table 5. Results of KPEG treatment of Syncon Resins soil--pesticides.[a]

Parameter	Untreated soil, ppb	Treated soil, ppb	Percent reduction
DDT	86.7	<0.016	>99.9
DDD	23.7	<0.016	>99.9
DDE	15.7	<0.047	99.7

[a] Results presented are averages of quadruplicate runs.

Table 6. Results of KPEG treatment of Syncon Resins soil--furans.[a]

Parameter	Untreated soil, ppb	Treated soil, ppb	Percent reduction
TCDF	8.03	<1.71	>78.7
PeCDF	22.9	<1.46	>93.6
HxCDF	8.77	<3.69	>57.9

[a] Results presented are averages of quadruplicate runs.

Table 7. Soil-washing results: Syncon Resins soil.[a]
(Soil particles greater than 2 mm in diameter)

		Treated soil[a]					
Contaminant	Untreated soil	Water wash	Percent reduction	Chelate wash	Percent reduction	Surfactant wash	Percent reduction
Metal							
Antimony	0.064	0.060	6.3	0.058	9.4	0.052	18.8
Arsenic	1.95	0.144	92.6	0.096	95.1	0.014	99.3
Barium	0.661	0.394	40.4	0.486	26.5	0.518	21.6
Copper	0.145	0.056	61.4	0.072	50.3	0.337	NR[b]
Lead	0.244	0.020	91.8	0.030	87.7	8.95	NR
Nickel	0.047	<0.027	>42.6	<0.026	>44.7	0.041	12.8
Vanadium	0.044	<0.016	>63.6	<0.015	>65.9	<0.014	>68.2
Zinc	0.910	0.305	66.5	0.434	52.3	0.493	45.8
Organic							
Pyrene, ppb	7880	2209	72.0	<1552	>80.3	<2500	>68.3

[a] Values in ppm, except where noted.

[b] NR = Not reported.

Table 8. Summary of organic results of thermal desorption of Berlin-Farro soil (average).

Parameter	Untreated soil, µg/kg	350°F, µg/kg	Percent reduction[a]	550°F, µg/kg	Percent reduction[a]
Volatile organics					
2-Butanone	290	343[b]	(18)	80	72
Trichloroethene	147	<23	>84	<25	>83
Tetrachloroethene	280	<23	>92	3	99
Toluene	483	19	96	27	94
Xylenes (total)	387	<23	>94	<25	>91
Semivolatile organics					
Hexachlorobutadiene	1,900[c]	430[c]	77	<3,300	NC[d]
Hexachlorocyclopentadiene	46,000	3,050	93	<3,300	93
Pentachlorobenzene	10,200	15,100	(48)	2,500	75
Hexachlorobenzene	105,000	250,000	(138)	47,000	55

[a] Reduction reported as percent change from initial concentration, not corrected by moisture. Increases in concentration are shown in parentheses.

[b] Compound detected in the laboratory blank.

[c] Estimated values are presented by the CLP laboratory.

[d] NC = Not calculated. The method detection limit of the analysis was exceeded by the laboratory; reduction cannot be calculated.

Table 9. Summary of organic results of thermal desorption of Old Mill soil (average).

Parameter	Untreated soil, µg/kg	350°F, µg/kg	Percent reduction[a]	550°F, µg/kg	Percent reduction[a]
Volatile organics					
Trichloroethene	2400	173	93	<25	>99
Tetrachloroethene	362	35	90	<25	>93
Toluene	152	43	72	57	63
Xylenes (total)	950	285	70	48	95
Semivolatile organics					
Aroclor 1260	2000	3000	(50)[b]	ND (100)[c]	>95

[a] Reduction reported as percent change from initial concentration, not corrected by moisture.

[b] Increases in concentration are shown in parentheses.

[c] ND = Not detected (method detection limit).

percentage of fine silt and clay, which should theoretically be harder to treat.

The percent reduction of semivolatile organic compounds from Berlin-Farro soil was slightly lower than for the volatile compounds. This is logical because of the higher vapor pressure of the volatiles. It is also noted that some of the semivolatiles show an increase in contaminant (values in parentheses) after thermal treatment. This is possible because moisture in the soil can evaporate while vaporization of the contaminant is insignificant. This could also be due to poor analytical results. More complete results on thermal desorption are given in Reference 2.

COMPARISON OF SUPERFUND SOILS (PHASE II) WITH SYNTHETIC SOILS (PHASE I)

Comparing these results on actual Superfund soils with the synthetic soils showed that the same trend in contaminant removals was accomplished on both types of soils. The synthetic soils gave a little higher percent removal than the actual Superfund soils. This is logical because the synthetic soils were spiked and tested with very little time for the contaminants to sorb deeply into the soil. The actual Superfund soils weathered for long periods; therefore, contaminant removal would be more difficult.

ACKNOWLEDGMENTS

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DISCLAIMER

The work described in this paper was funded by the U.S. Environmental Protection Agency. However, the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

PRE-TREATMENT OF HAZARDOUS WASTE

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ABSTRACT

The pre-treatment of waste is effected by a new method at KEMIAVFALL's reception and holding station in Malmö, Sweden. The purpose of the pre-treatment is to convert solid and pasty waste into pumpable waste. The types of waste most immediately applicable are lubrication greases, bituminous products, paints and glue waste. The solid and pasty waste are converted into emulsified form together with waste oil or solvent waste in specially designed grinding equipment. The resulting product, a so-called dispersion, can thereafter be conveyed further for final incineration. The advantages of the system are numerous. Since waste in drums is converted into a pumpable state for further transport in tank carriers, stock holding and transport of drums is reduced. Well-defined mixes can be produced by suitable mixture and dispersion. The final incineration at SAKAB, with its rotary kiln unit, or other authorized recipient plants can be better controlled and governed, at the same time that the capacity is utilized to a greater extent.

INTRODUCTION

KEMIAVFALL is a company which deals with the collection, transport, pre-treatment and storage of hazardous waste. KEMIAVFALL is a sub-division of SYSAV (Southwest Scania Waste, Inc.), which in turn is owned by a number of municipalities in southern Sweden. KEMIAVFALL operates at cost.

The Swedish model for handling hazardous waste divides the responsibility among industry (i.e., the waste producer), the municipalities and the Swedish State. The waste producer is expressly responsible and obliged to declare and package his waste and to deliver it to the municipality for further transport. He is also totally responsible for the contents of the waste and as the waste producer, he shall also assume all the expenses for the treatment. The handling of hazardous waste is prescribed in a special regulation.

Based on the Public Cleansing Act, the municipality is responsible for collecting and transporting hazardous waste, thereby creating coordinated and controlled handling. It should be noted that this naturally does not imply that the municipality treats waste itself. It can very well be done by hiring contractors. In order to acquire a sufficiently large base and the proper competence, collaboration among the municipalities is imperative, as in the case of KEMIAVFALL, which belongs within a commonly owned corporation.

The Swedish State is responsible for the final treatment of waste in part through its own waste corporation SAKAB, in part through other companies which have been given special license.

A proposal for new legislation that would place full responsibility for transportation and treatment on the municipalities has recently been made.

The State through its Environmental Protection Board also provides definitions of what is considered hazardous waste. It should be noted that at the present, no international convention and definition of what constitutes hazardous waste exists, a fact which at times can make information in these issues difficult to understand and even misleading.

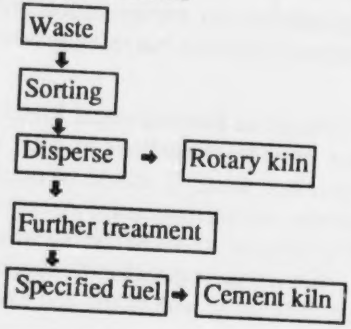
PURPOSE

One of the biggest problems at the present time in Sweden, as in many other countries, is that the capacity for the final treatment of hazardous waste is too limited. This is because industry's internal treatment of its own waste, for both technical and public opinion reasons, has not developed according to plan. At the same time, waste, which previously was handled more or less illegally, is now being taken care of more and more; this has led to an increased volume of hazardous waste. Industrial measures aimed at decreasing the production of hazardous waste material have on the whole proved to be of limited value so far, and have partially been counterbalanced by the increased total industrial production. All in all, this means that greater and greater amounts of hazardous waste cannot be treated.

Traditionally, much waste is treated in oil drums, at least in Sweden. This means that at the final destruction, the drums are often burned whole with their waste substances in for example the rotary kiln unit operated by the government corporation SAKAB.

Our hypothesis is that through pre-treatment of certain types of waste aimed at converting solid and pasty waste to pumpable waste, the capacity utilization in traditional rotary kiln units could be increased. In addition, a fraction of the waste after more pre-treatment could be treated and incinerated, for example as a specific fuel for the cement industry.

Principle Scheme



APPROACH

The following description and results concern the first step: a relatively simple pre-treatment followed by incineration in a rotary kiln. The report is based on practical experience from existing installations. In connection with this, a second step requiring further pre-treatment and the possibility of preparing a specified fuel is also reported on. Developmental work is in progress in this area, but full-scale production is not operational as yet.

Types of waste

Those types of waste which are applicable for pre-treatment in this context are those solid and pasty ones suitable for thermal treatment: certain types of waste oil, bituminous products, solvent waste, lubrication greases, paint, glue, and varnish, for example, which are usually handled in drums.

Technique

The necessary technical equipment consists of a newly developed "dispersion module". The drums are handled and emptied into a tank, where the contents are mixed with so-called dispersion solution, usually light oil and solvents. The waste is pumped and decomposed in a special aggregate until an emulcified ("dispersion") form is achieved, thereby the name. The ratio of dispersion solution to waste is c.1:5.

The capacity for creating a dispersion is decided first of all by the speed with which the drums can be emptied. The dispersion aggregate per se can normally treat several tens of cubic meters per hour. The rate for emptying the drums so far is c. 20 drums at a time, equalling 4 cubic meters/hr.

Flow Scheme

Waste classification
Analysis
Storage
Drum handling
- opening
- emptying
- cleaning
Dispension
- with oil/solments
Storage
Transportation
Incineration

Specific details

The main purpose of pre-treatment is to convert solid waste to a pumpable condition. This facilitates further transport and treatment. However, this is not enough. The final mix must furthermore meet certain previously determined criteria regarding energy content, heavy metal content, etc. Not until then can the dispersion waste be treated as a special product and be transported directly into and incinerated in, for example, a rotary kiln.

From the above it is clear that great exactness must be followed when taking samples or choosing the waste which is to be dispersed. The necessary knowledge does not always have to be collected by sample taking and laboratory analysis but can equally well be obtained through a closer record of the origin of the waste, he type of production, etc. Thus, by an intelligent application of chemical knowledge, enough information can be obtained to prevent the inclusion of certain particularly polluted types of waste. Knowledge of what is to be mixed and dispersed thus concerns not only the amount of heavy metals, halogens like chlorine and bromine, etc., in the waste in question, but also a chemical/technical judgement of the risks involved in joint storage effects, in the form of polymerization or other undesirable results.

The following items indicate the demands made on the homogenized waste:
Total halogens max. 1%, of which bromine 0.1%
Chromium max. 1000 mg/l
Lead max. 2000mg/l
Total alkali metals max. 500 mg/l
Cadmium trace
Quicksilver trace
PCB max. 50 mg/kg
Particles max. 10 mm
Heat value 16-20 MJ/kg
Pumpability Pump time when flowing in 3" pipe at least 10 cubic meters/hr

Storage/transport

The dispersion waste is temporarily stored in tanks and thereafter transported by tank carriers to the final treatment plant. This waste will gradually settle and therefore in certain cases, circular pumping must occur during temporary storage; in any case, the length of time from the dispersion to the final delivery must be kept as short as possible. Even transport by rail can be possible.

Treatment of left-over drums

The drums which are emptied are provisionally cleaned. In the cases when the drums are reused within the plant, for example for packing cans, etc., no additional cleaning is required. The remaining drums are compressed and deposited as hazardous waste. In order to recover scrapped drums, further chemical/physical cleansing must take place.

Installations

Dispersion aggregates are now operative in three places in Sweden, one in direct connection with the SAKAB complex, one outside of Stockholm, where the plant is run by a private contractor and is located c. 250 km. from SAKAB, and one at the KEMIAVFALL plant in Malmö, c. 500 km. from SAKAB.

Final treatment

Up to now, all experience is based on the final treatment by thermal incineration in rotary kiln units. Here the dispersion waste is treated like sludge and with its medium-good heat value is laid like a base load in the system. In this way both internally and externally produced dispersion are received and incinerated without any particular delay. From the point of view of incineration, it is obvious that the homogenized, pumpable waste is preferable to the drums. The capacity in the plant is increased at the same time that the incineration effectiveness can be kept high. This latter advantage means lower discharge and the former, a more cost-effective handling.

PROBLEMS ENCOUNTERED

Operational experiences taken from the three existing installations cover a relatively short period of time: The oldest plant has been in operation for c. two years and the other two, c. one year.

The following problems have been observed:

- * Difficulty in choosing drums whose contents will be dispersed
- * Spillage when emptying the drums
- * Long emptying time for "tough" waste
- * Somewhat unpleasant work environment.

The main problem stems from the preparation of the dispersion. Transport and final treatment appear to have few problems.

RESULTS

Experiences to date have shown that pre-treating by dispersion provides:

- More effective transportation, by replacing regional and long distance drum transport with tank carrier transport, providing a greater effective transport capacity.
- More effective incineration, when the whole drum, which must itself also be warmed up and contains solid and half-solid waste, is replaced by incineration of a liquid material, which on the whole means higher capacity, better incineration characteristics and there with lower discharge.
- More effective resource utilization of drums, which can be reused or recovered as scrap metal after cleaning.
- Lower total costs for both transport and final incineration, including naturally the extra costs for the pre-treatment.

FUTURE DEVELOMPENT

Up to now all experience has been based on final incineration in rotary kilns. As implied in the introduction, one of Sweden's biggest problems in this area is the crying need for sufficient final treatment capacity. Due to this, on-going research aims at developing a second pre-treatment step: through filtering and other efforts, separating permanent pigments and particles from paint waste for example, and adjusting the heating value to a specified fuel product with prescribed energy values, heavy metal content, etc. Such a reworked waste, while maintaining requirements for an environmentally positive incineration, should be able to be finally destroyed in, for example, cement kilns or certain other industrial heating units. In this way, one gains a considerably higher potential for a diversified final utilization. It should be observed however that such handling to the greatest extent possible must be coordinated with an extensive check of both the mixing equipment and the capacity and environment values at the final treatment plant. This is necessary, as an inadequate handling of the dispersion and pre-treated waste can lead to very unpleasant consequences. This is easily understood, since it can obviously be very tempting to include certain pumpable waste which has very high destruction costs, for example PCB waste, when making the dispersion.

In this area of development with second-stage pre-treatment, a considerably part of the dispersion material - 30–40% - will be separated as solid material. In order to achieve the capacity-heightening effect, it is obviously not a good idea to have the final incineration in a rotary kiln unit, as the waste is comprised chiefly of inorganic and solid materials. The goal here is to isolate this waste for deposition through some type of solidifying process.

Disclaimer

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HYDRAULIC JETT MIXING - VERSATILE TOOL FOR HAZARDOUS WASTE TREATMENT

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ABSTRACT

Many of the problems presented in most hazardous waste treatment processes are the result of being unable to sufficiently mix the waste stream with the solid, liquid or gas reactants required to provide treatment. This paper details the development of a mixing system that through the action of hydraulic jetts formed by a nozzle ring mixer configuration produces an extremely turbulent mixing action by the formation of a hydraulic venturi. The action of this venturi results in the aspiration of considerable volumes of air through the bore of the unit. Experimentation has proven that in addition to the oxygen transfer capabilities first evidenced by the unit, sufficient volumes of air are drawn through the unit to effect stripping of entrained and dissolved gases and volatile organic compounds (VOCs).

The development of the hydraulic jett mixing concept has to this point led to four separate applications in waste treatment processes. They are metals removal from solution through pH adjustment and oxidation, more efficient reagent mixing, high efficiency dry reagent mixing directly into a waste stream and air stripping of gases and VOCs from solution. This versatile piece of equipment attains its treatment efficiency because it was designed to enhance every aspect of mixing producing a high efficiency mixer. Extremely turbulent flow regimes are produced not only within the bore of the unit, but also within the jett streams as they leave the nozzles as evidenced by the streams' high Reynold's numbers. Additionally, the hydraulic flow path design reduces losses through the mixer to allow for high efficiency mixing at low heads.

INTRODUCTION

Efficient mixing of reactants into a waste stream has always been a problem in that there has been no mixer capable of combining all the elements of enhanced mixing into a single piece of equipment. Through the development of a mixing system for the mining industry to treat acid mine water containing heavy metals, a versatile new hydraulic jetting static mixer has been developed that has no moving parts and a clean bore with no internal components. As a result, this patented unit (U.S. Patents #4,474,477 & #4,761,077, with Other Patents Pending) can mix slurry-laden waste streams as well as clear water streams.

The main goal of the development of the hydraulic jett mixer was to reduce the size of the tankage required for an acid mine drainage (AMD) treatment plant through development of a static mixing device that could coincidentally aerate the treatment flow. This process equipment being developed would simultaneously adjust the pH and oxidize the metals allowing formation of the hydroxide sludges required for sedimentation and removal of the metals from the treatment stream. In effect, the device eliminates two reaction tanks, the neutralization/mixing tank and the aeration tank.

Further refinement of the delivery system allows many dry solids, such as hydrated lime or soda ash, to be directly injected into the treatment stream. As was found during the initial testing of the hydraulic mixing system, dry hydrated lime could be directly mixed into the acid treatment stream for pH adjustment. Not only could sufficient pH adjustment be attained, proving the concept of rapid direct injection of dry reagents, but further testing proved the units could produce milk of lime solutions extremely quickly. This allows batch tanks for existing lime solution injection style treatment systems to be downsized.

The oxidation capabilities of the hydraulic jett, as evidenced by its precipitation of high concentrations of metals from solution, led to investigation of the unit's capabilities to strip dissolved gases and volatile organic compounds from solution. Most easily stripped are dissolved and entrained gases, such as carbon dioxide, methane or radon.

Stripping of the volatile organic compounds with the hydraulic jett is somewhat harder due to their lower Henry's Numbers. For example, tetrachloroethylene (PCE) only has a removal rate of 75-78% on a single pass, however, multiple passes, five recycles, achieve greater than 98% removal efficiencies with a fourth generation design. While more passes may be required to achieve sufficient removal rates, this is overcome by the size of the unit, less than 6' tall, and its use of aspirated air for stripping.

As with the other hydraulic jetting applications, intimate mixing of the gas stream with the organic chemical-laden water provides the driving force to remove the organics from solution.

PURPOSE

The treatment process for acid mine drainage (AMD) is straight forward, raise the pH of the liquid, then aerate to precipitate the metals from solution. Traditionally, a flash mixer in a separate tank receives a lime slurry to mix with the incoming acid water flow. The thirty second to five minute retention period insures that a neutralized effluent is discharged into the aeration tank where the metals, which have changed state, can be oxidized and form a hydroxide precipitate during the additional twenty to thirty minute retention period. (3,5,8)

Development of an enhanced mixing system would produce a more efficient and cost effective treatment process. The basic parameter selected for enhancement was the generation of additional interface surface area. The other design consideration was to produce a mixer that eliminated the large tankage volume generally devoted to the mixing and aeration portions of the treatment process.

The initial research & development of what came to be the hydraulic jett started with the premise that the mixer would be of a static design and would utilize the velocity generated by passing the flow through nozzles specially designed to greatly enhance the turbulence within the contacting chamber of the mixer. (1,6,7)

APPROACH - ACID MINE DRAINAGE (AMD)

With a mixer designed to produce neutralization of an acid stream along with the capability to inject air to effect oxidation of the metals present within the acid stream, the next step was to field test the equipment to insure that it could be scaled up to process flows in excess of 500 gpm.

The original field testing was divided into two components: the first consisted of testing at an acid water flow of 100 gpm, while the second was at 800 gpm. The trial used a side stream from an acid mine water source in West Virginia and discharged into the holding basin prior to the existing acid mine water treatment plant.

The trial set-up included stainless steel submersible pumps, both liquid and dry solid delivery systems and 2" and 8" hydraulic jett units.

The test started with the 2" hydraulic jett operating at 100 gpm through the 1/8" nozzles. (Figure 1) The milk of lime slurry was injected through the throat of the unit to contact the acid water stream within the bore. A blower supplied low pressure air for oxidation of the metals after neutralization of the acidity.

Upon completion of the testing with a lime slurry as the neutralizing agent, the next step was to determine if the hydraulic jett mixer could take a dry solid feed and effect the neutralization reaction within the short mixing period available. To accomplish this a converted "rock duster" was used to pneumatically convey powdered hydrated lime into the bore through the throat of the mixer. As with the previous test a low pressure air supply was used.

The next stage of the testing was to operate at a 800 gpm flow and to attempt to duplicate the results obtained with the testing at 100 gpm flows. In this portion of the testing an 8" hydraulic jett mixer (Figure 2) was used. This unit used 3/8" nozzles. Both lime slurry and dry lime injection was performed along with injection of liquid sodium hydroxide (NaOH).

PROBLEMS ENCOUNTERED - AMD

Injection of the lime slurry into the mixer produced no problems even at high feed rates. However, pneumatic conveying of a dry lime suspension resulted in a calcium carbonate build-up created by backsplashing of the jetts. This build-up occurred in both size units and steps were taken to eliminate the problem by relocating the air entrance to the mixer. Further design changes resulted in the back of the mixer bore being left completely open allowing an air flow to be aspirated into the bore preventing backsplashing of the liquid.

RESULTS - AMD

The 2" hydraulic jett mixer was designed to pass 100 gpm through 72 nozzles placed in the wall of the center bore. Two additional chambers, each containing an additional 48 nozzles, were located before and after the main injection ring. These chambers were for injecting air or additional flows into the bore of the mixer.

With the lime slurry addition to the acid water flow, the hydraulic jett mixer was able to neutralize the acidity present in the process stream and raised the pH from 3.5 through to near 12 at successive levels of test-

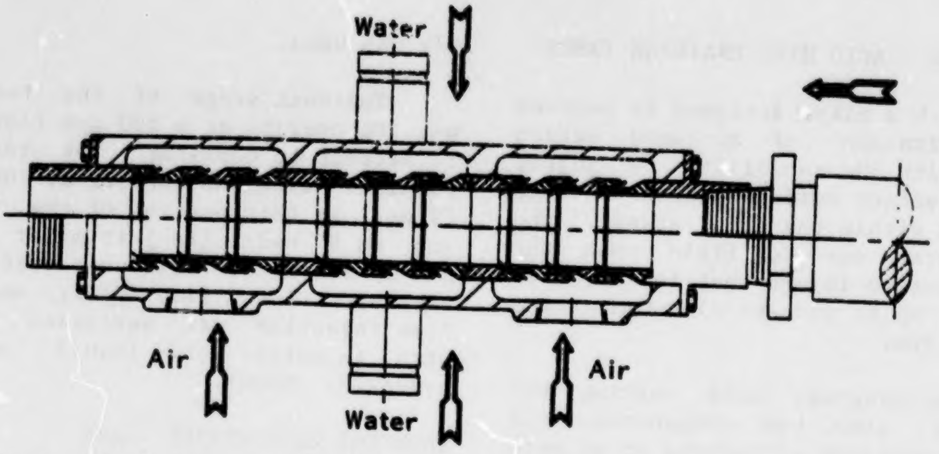


Figure 1: First Generation Hydraulic Jett Mixer

Figure 2: Acid Mine Drainage Hydraulic Jett Mixer

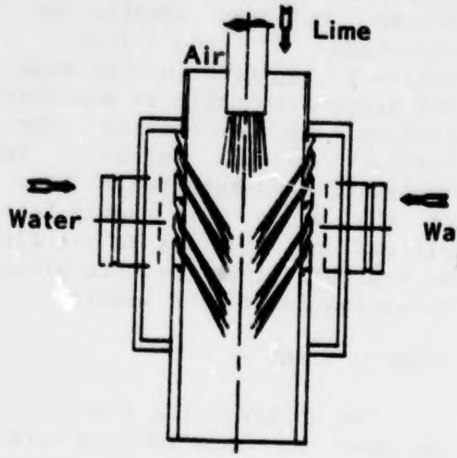
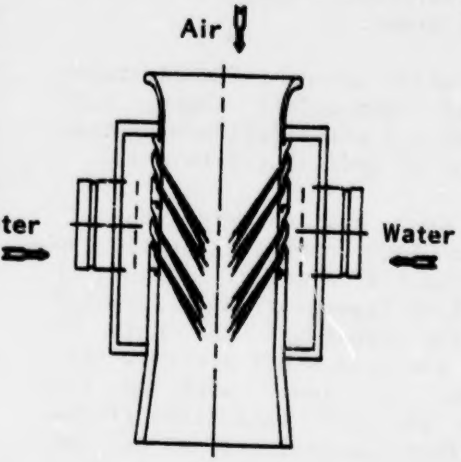


Figure 3: Air Stripping Hydraulic Jett Mixer



ing. This was especially impressive in that the total residence time within the mixer was 0.2 seconds prior to discharge. The stochiometric lime additions produced results that closely followed the titration curve for the mine water being tested. Additionally, the air volume injected was sufficient to oxidize all the iron present in the mine water. Iron concentrations in excess of 500 mg/l (80% ferrous, 20% ferric) were present in the flow and were precipitated in the form of ferric hydroxide to pH levels of 10.5.

The next step of the testing of the 2" unit was to pneumatically convey powdered hydrated lime into the bore of the unit to mix directly with the acid water. As with the lime slurry, each level of lime addition drove the pH up in accordance to the titration curve reaching a maximum pH of 11.3. Again, the neutralization reaction was complete as the liquid left the unit as evidenced by no further pH rise. Oxidation and precipitation of the metals was also driven to completion upon sufficient increase in pH.

The next series of tests, which incorporated the design changes developed from the testing of the 2" mixer, was to determine the scale-up capabilities of the hydraulic jett concept. An 8" mixer passing 800 gpm using the same nozzle configuration as the 2" unit, except for the nozzle diameter, was tested.

The major difference between the units (Figures 1 & 2) was to open the back of the 8" unit's bore. As was described in the Problems Encountered section, the need to eliminate the backsplashing led to the discovery that large volumes of air are aspirated into the bore by the venturi action of the hydraulic jetts. The AMD units incorporated this design change throughout the remaining testing.

The 8" unit produced the same results as the 2" unit in terms of neutralization and oxidation efficiency for lime slurry injection, dry hydrated lime feed and with this series of tests, liquid caustic.

However, in this series of tests, the air used for oxidizing the metals was not obtained by low pressure injection, but through air aspirated co-current with the water flow. The oxygen mass transfer mechanisms produced are so efficient that the dissolved oxygen concentration was driven from 1 to 2 mg/l to saturation levels of over 11 mg/l with just the single pass through the hydraulic jett mixer. The mine water temperature during the trial was in the mid 50's F. (1,4,7)

As a result of this series of tests the hydraulic jett mixing system has been commercially applied in acid mine drainage treatment plants in West Virginia and Ohio. These plants have produced considerable savings as the cost of treatment has dropped from $0.54 per thousand gallons for conventional lime and aeration treatment to $0.17 per thousand gallons with the hydraulic jett system. (4)

APPROACH - SLURRYING SOLIDS

From review of the results of the hydraulic jett mixer's AMD tests, it was felt that lime could be slurried into a water stream using the hydraulic jetts. A series of tests were performed to verify the potential application.

Initially, to test the premise, the 2" hydraulic jett mixer used in the AMD testing along with a further modified "rockduster", were placed at a mine site in West Virginia to produce a "milk of lime" slurry from dry hydrated lime.

A second test was performed at a New York State electric utility where a specially designed hydraulic jett unit was installed to reduce the time required to slurry a tanker truck load of hydrated lime. Subsequent tests at the same site have been performed aimed at producing higher slurry concentrations and in batching slurry production. (2,7)

PROBLEMS ENCOUNTERED - SLURRYING SOLIDS

Two problems were encountered during the development phase of the hydraulic jett for the application of producing slurries/solutions, primarily milk of lime, from hydrated lime. They were 1) balancing the aspirated and conveying air volumes, and 2) insuring the wetting of all the dry solids entering the unit.

The first problem presented itself when the air volumes being used to convey the dry hydrated lime from its silo exceeded the air volume the hydraulic jett unit could aspirate and resulted in blowback of lime solids from the bore. The problem was solved by balancing the velocities of the two air streams to insure a constant inward motion of the air flow.

The second problem occurred when milk of lime slurries in excess of 10% solids by weight were being made. Wetting of all the solids needed to be insured to attain complete mixing. This problem was solved by reconfiguring the jett nozzles.

RESULTS - SLURRYING SOLIDS

The production of lime slurries with the hydraulic jett mixing system is a simple process in which powdered hydrated lime is pneumatically conveyed or dropped into the back bore of the jett unit. (Figure 2) It is contacted with a set volume of water, where it is initially wetted and then slurried by successive jetted flows within the bore of the unit.

The hydraulic jett mixers have been used to make "milk of lime" slurries in concentrations ranging from 5% to 25% solids by weight. The main advantages in using this type of mixer are the time factor and dustless operation of the units.

Testing at a New York State utility produced a system in which the time taken to make up the 750 gallon milk of lime "day tank" was dropped from approximately four hours to less than ten minutes, while eliminating the lime dust problem inherent in their traditional lime slurry production.

The production of lime slurries using the hydraulic jetts is being commercially applied with significant customer cost savings in operator time, maintenance time and the more efficient mixing allows greater efficiency in the lime usage. (2)

APPROACH - AIR STRIPPING

Review of the results of the development testing for the acid mine water treatment process showed that an extremely efficient aeration device had been produced. As placing a gas (oxygen) into solution was easily accomplished, the premise was forwarded that the same hydraulic jett principle could just as easily remove gases from solution.

The same mixing action that produced the large surface areas needed for mixing when combined with the large air flows aspirated through the unit would act similarly to existing air stripping technology, such as, packed, counter-current air stripping towers.

A new test unit was made to attempt to remove PCE and radon from a groundwater source. Further modifications (Figure 3) of the hydraulic jett design were made to increase the air handling capacity of the unit.

A total of three tests were performed with the air stripper version of the hydraulic jett mixer. One removing PCE and radon from groundwater, one removing PCE from a spring source and the third removing methane and hydrogen sulfide from a groundwater source. All these tests were on existing potable water supplies.

PROBLEMS ENCOUNTERED - AIR STRIPPING

The premise that air stripping with the hydraulic jett would be as easy as aerating with the device, unfortunately did not hold. The first tests, while showing promise of results to come, did not provide superior removal efficiencies on a single pass through the unit for volatile organic chemicals, however, dissolved radon & methane gases were readily removed from solution.

Modifications of the hydraulic jett design to increase the air volume entrained by a single unit were made and the units were retested.

RESULTS - AIR STRIPPING

As previously described three major tests removing PCE, radon and methane were performed in 1987-88 to verify the removal efficiencies of the hydraulic jett when used to air strip.

The first test was performed at a well site in northeastern Pennsylvania contaminated with tetrachloroethylene (PCE) and radon. A trial was set up for operation of a 2-1/2" Twin hydraulic jett unit operating on a single pass of the flow from the well pump. Discharge of the flow into a receiving tank allowed an 18" free space above the water for volatile separation from solution. The unit used produced a volumetric ratio of air to water of 17:1.

As the results listed in Tables 1 & 2 show the hydraulic jett unit used for this first test handled PCE concentrations ranging from 10 to 15 ppb in a flow of 120 gpm on a single pass at removal efficiencies ranging from 55 to 60% for temperatures over 20 F. There was a significant drop in removal efficiency with the advent of colder (20 F) weather. Average removal efficiencies were near 40% for that part of the testing. This represented about a 36% drop-off in removal efficiency for the colder weather.

Table 1: PCE Removal Single Pass

Sample	Source	Result	Reduction
12/11	Influent	15 ppb	
	Effluent	6 ppb	60%
12/12	Influent	12 ppb	
	Effluent	5 ppb	58%
12/19	Influent	10 ppb	
	Effluent	6 ppb	40%
12/20	Influent	11 ppb	
	Effluent	7 ppb	36%

Radon levels in the water stream ranged from 1500 to 1900 pCi/L. An average 90% removal rate was attained for 20 F operation with only a drop-off to 85.5% for cold weather operation.

Table 2: Radon Removal Single Pass

Sample	Source	Result	Reduction
12/11	Influent	1910 +/-100	
	Effluent	180 +/- 45	91%
12/12	Influent	1675 +/- 85	
	Effluent	188 +/- 40	89%
12/19	Influent	1518 +/- 82	
	Effluent	213 +/- 40	88%
12/20	Influent	1752 +/- 80	
	Effluent	303 +/- 40	83%

Radon levels measured in picocuries per liter (pCi/L).

The results from the first test showed that improvements could be made to the unit to enhance the removal efficiencies by increasing the air volumes and recycling the flow through the unit. Table 3 shows the results of a recycle test on PCE removal from a contaminated spring in central Pennsylvania.

As indicated the PCE levels could be dropped considerably below the MCL of 5 ppb with three passes through the hydraulic jett with approximately 99% removal with five passes. This unit had an increased air flow that produced a volumetric air to water ratio of 28:1.

Table 3: PCE Removal Recycle

Sample	Result	Reduction
Influent	39.1 ppb	
Recycle 1	12.3 ppb	73.7%
Recycle 2	5.7 ppb	85.4%
Recycle 3	2.0 ppb	94.8%
Recycle 4	1.0 ppb	97.3%
Recycle 5	0.4 ppb	98.9%

As a result of these tests the hydraulic jett air stripping process has been issued an innovative permit by the DER in Pennsylvania for use in volatile organic compound removal for potable water treatment.

One other on-going test is in New York State in which a methane and hydrogen sulfide contaminated well is being successfully treated for potable use. In addition to producing a palatable water, the unit is also oxidizing the iron present in the flow eliminating the previously required potassium permanganate addition. This unit is in operation on an emergency permit from the New York Department of Health.

The hydraulic jett has proven to be a versatile piece of equipment that has considerable potential in the treatment of contaminated water sources. Its capabilities are accomplished through the high turbulence generated within the jetted nozzles which produces extremely large surface areas for contacting the water with the aspirated air stream.

ACKNOWLEDGEMENTS

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DEMONSTRATION OF TECHNOLOGIES TO REMOVE CONTAMINATION FROM GROUNDWATER

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ABSTRACT

The Westinghouse Hanford Company has been testing various technologies for decontaminating groundwaters and liquid effluents. The results of preliminary testing of three technologies are reported. The technologies are iron coprecipitation/filtration, supported liquid membranes, and reverse osmosis. The processes were tested to determine their capability to remove uranium, chromium, nitrates, and technetium. All processes removed contaminants to less than maximum contaminant limits. The secondary waste volumes were estimated for each process. The supported liquid membranes secondary waste volume was the smallest, followed by iron coprecipitation, and the largest volume was created by the reverse osmosis process.

INTRODUCTION

The Hanford Site at Richland, Washington, is operated for the U.S. Department of Energy (DOE) by the Westinghouse Hanford Company (Westinghouse Hanford). Until recently, an acceptable method for disposing of water containing small amounts of contaminants was to discharge the water to underground cribs. Forty years of operation at the Hanford site has resulted in the contamination of some of the groundwaters with such compounds as uranium, chromium, technetium, and nitrates. The current goal of Westinghouse Hanford and the DOE is to cease disposal to the soil column and to investigate the removal of the contaminants from the groundwaters. The diverse nature of the processes at the Hanford Site has created groundwaters at different locations with different contaminants, thus increasing the difficulty of implementing remedial actions in a cost-effective manner.

Westinghouse Hanford has a program to demonstrate and develop technologies that will remove contaminants from groundwaters and to determine the volume of secondary waste that will be generated so that it can be minimized. Reverse osmosis and coprecipitation with iron are two water treatment technologies that are being tested with groundwater samples to demonstrate the purity of water that can be produced. Initial testing is also designed to identify potential problems and to provide information to help evaluate these processes.

In addition, a new, emerging technology, supported liquid membranes (SLM), is being developed. The SLMs have the potential to be a very powerful tool in restoring groundwaters to their uncontaminated state.

A primary criterion for a potential treatment process is that it produce a relatively small amount of secondary waste. One purpose of this testing was to determine the secondary waste volume generated by each of these processes.

The capability of the processes that were tested to remove contaminants from groundwater will be evaluated by comparing final contaminant concentrations to the maximum contaminant limits (MCL).

Iron Coprecipitation/Filtration

Iron coprecipitation is a process that is used in the Uranium Mill Tailing Remedial Action (UMTRA) program to remove radium, uranium, and other contaminants from the surface runoff wastes generated during remedial action (5). It is also used at the Oak Ridge Y-12 Plant to remove uranium from nitrate-containing wastes (2).

Iron is added to the stream and then precipitated with the contaminants when the pH of the solution is raised by the addition of lime or sodium hydroxide.

Once the precipitation has occurred, the contaminant-containing solids must be separated from the water. This can be done using microfiltration as at the UMTRA site at Lakeview, Oregon, or by settling as used at the Oak Ridge Y-12 Plant. Coprecipitation is a process that removes metal ions, however, it will not remove nitrate ions, which are a serious contamination problem in some of the groundwaters at Hanford.

Supported Liquid Membranes

The SLM technology has been investigated on a laboratory scale for the past 20 years and on a very limited pilot scale for the past 10 years. There are two types of liquid membranes: emulsion membranes and SLM. Only tests of SLM have been performed at Westinghouse Hanford.

An SLM is an organic phase that is held by capillary forces within the pores of a microporous polymeric membrane. A detailed description of SLM can be found in Danesi et al. (3).

SLM have several advantages over conventional solvent extraction and water treatment technologies as follows:

- Very low solvent requirements
- Improved selectivity
- Reduced cross contamination
- Recovery of species present in low concentrations
- Low secondary waste volumes
- Nitrate removal.

The SLM development at Westinghouse Hanford is a joint effort with the Argonne National Laboratory (ANL) and has focused on the problem of removing uranium and nitrate from groundwater. An extraction system for removing uranium has been identified and tested at ANL (1, 2); the results of a demonstration of this system using a 2.2 square meter (m^2) SLM module and a sample of contaminated groundwater are reported here.

Reverse Osmosis

Reverse osmosis is a separation technology used for very difficult separations (i.e., salt from water) and can produce highly purified water. However, the rejection of salts is a function of the salt concentration in the feed. In order for reverse osmosis to compete as a process for cleaning groundwater, it must produce a small secondary waste. This means that the feed will become very concentrated in dissolved solids, and the percent rejected may decrease. The goal of these tests is to reduce the contaminants to below MCL. These levels are very low; therefore, a small decrease in rejection of a contaminant may cause that contaminant to exceed the drinking water standards in the permeate.

The combined disadvantage and advantage of reverse osmosis is that it removes all of the ions present. This is a disadvantage because the secondary waste volume is increased by ions, such as sodium and calcium, that do not need to be removed. It is an advantage because ions, such as nitrate, are also removed. Most of the contaminated groundwaters contain nitrate in excess of the MCL.

Secondary Waste

The volume of secondary waste that is generated in the cleanup of a groundwater or plant effluent is very important to the economic viability of a process. This is especially true when the secondary waste must be treated as a hazardous waste or mixed hazardous/radioactive waste and disposed of in accordance with applicable State and Federal laws. Therefore, the testing of these processes is not only to evaluate their capability to reduce contaminants to MCL, but to help estimate the amount of secondary waste that will be generated during processing.

The secondary waste volume for each process that is tested will be one of the process characteristics used to determine the process with the best capability to economically decontaminate groundwater.

PURPOSE

Development is needed to provide engineering and management with the information necessary to select processes that will decontaminate groundwater while generating a minimum amount of secondary waste.

The diverse nature of the contaminated groundwaters and liquid effluents make the testing of various process options necessary to be able to select the process or processes with the capabilities to reduce the contaminants to the required levels. The levels used for evaluation were the MCL. The MCL for the contaminants of concern in this study are given in Table 1.

Table 1. Maximum Contaminant Limits (4).

Contaminant	Maximum contaminant limits
Technetium-99	900 pCi/L
Uranium	10 ppb
Chromium	50 ppb
Nitrate	45 ppm

APPROACH

The three technologies described above were tested using contaminated groundwater. The scope of the testing was limited to demonstrating the capabilities of the technologies and to providing the information necessary to allow the estimation of the secondary waste volumes.

Iron Coprecipitation/Filtration

The iron coprecipitation/filtration tests were performed on three contaminated groundwaters. The groundwaters and the contaminant levels are given in Table 2.

Table 2. Contaminant Levels in Groundwater Used in Testing.

Groundwater	U (ppb)	Cr (ppb)	Tc (pCi/L)	Nitrate (ppm)	Cyanide (ppm)
No. 1	3460	--	786	38	--
No. 2	140	190	--	273	--
No. 3	--	--	4300	368	2.2

Samples of these groundwaters were placed in 55-gallon drums and transported to the laboratory for testing. The apparatus used for testing consisted of a feed tank, a filtrate tank, a pump, and a crossflow filter that was a 1-inch tubular polyfluorotetraethylene microfiltration membrane 3.7 meters (m) long. Several tests were conducted with each groundwater to try to identify the conditions under which maximum decontamination could be realized.

Supported Liquid Membrane

The supported liquid membrane process was tested with groundwater number one. Two separate tests were conducted using an apparatus that contained two membrane modules. Each membrane module contained 2600 microporous hollow fibers. The hollow fibers were made of microporous polypropylene and had an inside diameter of 0.6 millimeters (mm). The internal surface area of each module was 2.2 m^2. One module was used to remove uranium from the groundwater and the other module was used to remove nitrate and technetium.

The SLM process for removing uranium from groundwater was developed at ANL (1, 2) for Westinghouse Hanford. This process uses an extractant that is 0.1 molar (M) bis(2,4,4-trimethylpentyl)phosphinic acid (H[DTMPePA]) in n-dodecane. The H[DTMPePA] is the active reagent of the commercially available Cyanex 272[1]. The H[DTMPePA] was selected because of the high distribution ratio for uranium and its selectivity for uranium over calcium and iron. The strip solution used in the uranium removal process is 0.1M 1-hydroxyethyl-1,1 diphosphonic acid (HEDPA).

The SLM process for removing nitrate and technetium uses 0.1M primene JM-T[2] in n-dodecane as the extractant. The primene JM-T is a product of the Rohm and Haas Company. The strip solution used was 0.5M sodium hydroxide (NaOH).

In the first test, 50 gallons of water were recirculated through the uranium removal module. In the second test, the treated groundwater from the first test was recirculated through the nitrate/technetium removal module.

Reverse Osmosis

The feed to the reverse osmosis test was groundwater from the same location as that used in the supported liquid membrane testing

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(1) Registered Trademark American Cyanamid Company.
(2) Registered Trademark Rohm and Haas Company.

(groundwater 1). The reverse osmosis system consisted of two feed tanks, a pump, a reverse osmosis membrane, assorted pressure gauges, flowmeters, a conductivity sensor, a temperature sensor, and valves. The membrane that was used in this test was a Filmtec FT-30, constructed of a thin film composite polyamide. It is a spiral wound cartridge and the dimensions are 1x16 centimeters (cm) with 2.1 m^2 of membrane area. The feed was to be concentrated until precipitation occurred or until the water flux dropped to 60% of the original value.

PROBLEMS ENCOUNTERED

The determination of contaminant concentrations in the groundwater samples after substantial amounts of the contaminants had been removed was a problem. This is true for both the radioactive and nonradioactive contaminants. One way this was countered was to take large samples and to concentrate them prior to analysis.

RESULTS

Iron Coprecipitation/Filtration

Uranium, chromium, and cyanide were successfully removed from the three groundwaters.

The results of these tests (summarized in Table 3) indicate that uranium and chromium can be reduced to below the MCL in groundwater. However, the treatment scheme for each groundwater will be different. In treating groundwater 2, sodium metabisulfite was added to the water prior to precipitation to reduce the hexavalent chromium to trivalent chromium. A treatment with sodium hypochlorite was used with groundwater 3 to destroy the cyanide.

In these tests, one contaminant was targeted for removal from each stream and in general was reduced to below the MCL for that contaminant. However, in several cases there were other contaminants in the stream that were not reduced to below their MCL. For example, the chromium in groundwater 2 was removed, but the uranium present was not reduced to less than the MCL. Through further testing, it should be possible to modify the process to remove most of the contaminants. The contaminant present in most of the contaminated groundwaters that cannot be removed by this process is nitrate.

Supported Liquid Membranes

The goal of runs with groundwater 1 was to reduce the uranium, nitrate, and technetium to less than their MCL. The MCL are given in Table 1. In the first run, the uranium was removed using 0.1M bis(2,4,4-trimethylpentyl)phosphinic acid (H[DTMPePA]) in dodecane. The results of these tests are given in Table 4. The uranium concentration in the groundwater was reduced from 3460 ppb to less than the MCL of 10 ppb in less than twelve hours. The technetium, nitrate, sulfate, and chloride concentrations did not change during the run.

The second run performed was to remove nitrate and technetium from the groundwater that had been treated in the first run to remove uranium. The membrane was 0.1M primene JM-T in dodecane and the strip solution was 0.5M NaOH. The results of this test are also presented in Table 4. The nitrate was reduced to half its original concentration in less than 20 hours, while the technetium was reduced to less than half of its original concentration in less than 4 hours.

Table 3. Summary of Coprecipitation/Filtration Test Results.

Contaminant	Percent removal	Final concentration range	Maximum contaminant limit
Uranium	88.6-99.9	1-7 ppb	10 ppb
Chromium	97.9-99.5	1-4 ppb	50 ppb
Cyanide	100	not detectable	N/A

Table 4. Uranium, Nitrate, and Technetium Removal Demonstration Results.

Time (Hr.)	Uranium[a] (ppb)	Technetium[b] (pCi/L)	Nitrate[b] (ppm)	Sulfate[b] (ppm)	Chloride[b] (ppm)
0	3,460	786	38.5	1,120	14.6
4	257	361	37.0	1,110	14.3
8	29.9	139	31.0	1,020	13.6
12	7.3	51	24.7	974	13.7
16	2.1	18	20.9	848	12.8
20	1.4	9	18.1	810	11.8
24	1.3	8	15.3	716	12.7
36	0.97	4	10.2	920	10.6
48	1.31	2	42.0	793	9.4
strip 48	31,200	11,600	358.0	8,420	78.8

a Run #1
b Run #2

It appears that the technetium was extracted faster than the nitrate. The pH of the groundwater was monitored during the run and when it increased to 2.3, additional sulfuric acid was added to ensure that sufficient hydrogen ions were present to transport the nitrate, as nitric acid, across the membrane. The data show that sulfate and chloride were also transported across the membrane.

A third run in which the modules were connected in series to remove the uranium, nitrate, and technetium simultaneously was conducted. The data for this run are not presented here. However, it is important to point out that the strip solutions used in the third run were the same ones used in the first and second run. That is, the uranium from approximately 100 gallons of groundwater was concentrated into 4 gallons, and the nitrate and technetium from 100 gallons was also concentrated into 4 gallons.

Reverse Osmosis

The feed for the reverse osmosis test was 770 gallons of groundwater 1. The concentrate stream was recycled through the membrane and the permeate was collected and sampled. After the concentrate stream had been processed through the membrane nine times, a precipitate formed that was determined to be calcium carbonate. Hydrochloric acid was added to dissolve the precipitate and processing was continued through five more membrane passes. The acid addition changed the test parameters considerably so results will be discussed as before acid addition and after acid addition.

The results before acid addition (Table 5) show that uranium and technetium were removed to well below the MCL. The analysis of the feed water showed 11 to 26 ppm carbon tetrachloride. None was detected (ND) in the permeate. However, there was not a corresponding increase in the concentrate stream, so the results are not conclusive. Ninety-two percent of the nitrate was rejected, which left a concentration of less than 3 ppm in the permeate stream.

After processing through nine passes the volume had been reduced from 770 to 88 gallons. This was calculated to be a recovery of 88.6%. The flux during the ninth pass was 83% of the original flux.

Rejection rates decreased for all three of the constituents measured after hydrochloric acid was added. This was expected since the salt passage through the membrane is a function of the concentration differential across the membrane. Usually this rate decreases gradually and makes very little difference in the overall percent rejection. However, the addition of hydrochloric acid changed the concentration of ions in the feed by a considerable amount, and rejection rates of all the constituents were affected. This was most noticeable in the technetium and nitrate results (compare Table 5 with Table 6). Concentrations in the permeate were still below the MCL in all cases.

After processing through fourteen passes, the concentrate stream had been reduced to about 31 gallons for an overall recovery of 96%. During processing through the fourteenth pass, the flux decreased to 60% of the starting flux. At this time the test was terminated.

Secondary Waste Volumes

One of the important criteria for judging the desirability of a treatment system is the volume of waste generated during the treatment process. The testing reported here was exploratory and was not extensive enough to optimize process parameters to minimize the secondary waste volume. However, to aid in the evaluation of this technology, an attempt has been made to estimate, based on the testing results, the volume of secondary waste. The estimated secondary waste volumes are presented in Table 7.

Table 5. Summary of Reverse Osmosis Test Results Before Acid Addition (Nine Passes).

Contaminant	Permeate concentration	Percent rejection	MCL
Uranium	4.9 ppb	99.9	10 ppb
Technetium	57.3 pCi/L	95.3	900 pCi/L
Carbon tetrachloride	ND	--	5 ppb
Nitrate	2.6 ppm	92.1	45 ppm

Table 6. Summary of Reverse Osmosis Test Results After Processing Through Fourteen Passes.

Contaminant	Permeate concentration	Percent rejection	MCL
Uranium '	7.8 ppb	99.8	10 ppb
Technetium	192.7 pCi/L	83.9	900 pCi/L
Carbon tetrachloride	ND	--	5 ppb
Nitrate	5.6 ppm	82.0	45 ppm

Table 7. Comparison of Secondary Waste Volumes for Iron Coprecipitation, Supported Liquid Membranes, and Reverse Osmosis.

Process	Secondary waste volume
Iron coprecipitation	0.4 gallons/1000 gallons of feed
Supported liquid membranes	0.1 gallons/1000 gallons of feed
Reverse osmosis	114 gallons/1000 gallons before acid was added 40 gallons/1000 gallons with acid addition

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Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

SOIL DECONTAMINATION WITH EXTRAKSOL™

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ABSTRACT

Polychlorinated biphenyls, polyaromatic hydrocarbons, oils, pentachlorophenols have been succesfully extracted from clay-bearing soil, Fuller's earth, oily sludge, activated carbon and gravel by the one ton per hour Extraksol™ unit.

The Extraksol™ process is a mobile decontamination technology which treats unconsolidated materials by solvent extraction. Treatment with Extraksol™ involves material washing, drying and solvent regeneration. Contaminant removal is achieved through desorption/dissolution mechanisms. The treated material is dry and acceptable to be reinstalled in its original location.

The process provides a fast, efficient and versatile alternative for decontamination of soil and sludge. The organic contaminants extracted from the matrix are transferred to the extraction fluids. These are thereafter concentrated in the residues of distillation after solvent regeneration. Removal and concentration of the contaminants ensures an important waste volume reduction.

This paper presents the process's operational principles and the steps involved in Extraksol's development with results of the pilot tests and full-scale demonstrations.

INTRODUCTION

Extraksol™ is a mobile decontamination process which extracts organic contaminants from unconsolidated materials such as soil, sludge, gravel, etc. Polar and non-polar contaminants are extracted from the soils by solvent washing through desorption / dissolution mechanisms. Treatment with Extraksol involves material washing and drying, which generates a decontaminated, dry soil, ready to be returned to its original location.

Extraksol™ has been developed and commercialized by the Sanivan Group to complement its hazardous waste treatment technologies. Initially developed to extract polychlorinated biphenyls (PCBs) from contaminated soil, Extraksol™ has since demonstrated to be an efficient solution to recycle sand, gravel, mixed soil and sludge contaminated with oils, greases, polyaromatic hydrocarbons (PAHs), chlorinated organics such as pentachlorophenols (PCPs) and other common organic pollutants.

Extraksol™ has been designed as a closed system (no gaseous or liquid discharges) which considerably reduces the volume of contaminants. The solvents used are non-chlorinated, non-toxic and non-persistent. Solvent regeneration is an integral part of Extraksol™ and is carried in parallel to the extraction activities. Solvent regeneration allows to associate the benefits of soil decontamination to the advantages of contaminant volume reduction.

Treatment of soil by extraction of the contaminants with a non-toxic, non-persistent solvent, is an elegant approach which provides an environmental recommendable solution; the contaminants are removed and contained without need to destroy the soil. Furthermore, since soil drying is part of the process, the treated, dry soil can often be returned to its original location after mixing with top-soil for revegetation.

Treatment of contaminated soil by solvent extraction has been first applied on an industrial scale in the Netherlands in 1983 and 1985. Large, fixed extraction plants were built to solve the problems of hydrocarbons and cyanides. Plants such as the Heijmans Milieutechniek B.V., HWZ Bodemsanering B.V., Ecotechniek B.V., Heidemij Milieutechniek B.V. and Mosmans Milieutechniek B.V. combined the techniques of coagulation/flocculation, sedimentation, flotation, high pressure jets, thermal washing and froth flotation, to decontaminate 10 to 30 tons of soil per hour (1, 2).

In North America, the tendency is to develop flexible, mobile systems which can treat the materials on-site. Available techniques employ organic solvents (both as low pressure liquids and critical fluids), amines, supercritical carbon dioxide as extraction fluids (3, 4, 5).

This paper describes the Extraksol™ process and presents the objectives and results of the pilot-scale work and of the various demonstrations conducted with the one ton per hour Extraksol™ unit on PCB containing soil as well as on other organic contaminants and matrices.

PURPOSE

In Eastern Canada, there is no alternative for PCB contaminated soil other than containment and securisation. Incineration of PCBs is not yet an accepted solution whereas biodegradation techniques are not available.

Solutions exist for other priority contaminants, but these are often not applied due to high treatment costs, NIMBY effects, extensive treatment periods, local regulations, etc. Often non-PCB sites will be rehabilitated by landfilling or encapsulating the wastes with or without previous fixation. To reduce costs, clean-up is often carried-out through solutions which are not really environmentally acceptable.

Based on these facts, the Sanivan Group had identified, in 1987, a pressing need for the development of an efficient, mobile, non- destructive, environmentally acceptable technology to treat PCB-contaminated soil and other non-consolidated materials.

Market studies had also revealed the need for a non-specific technology which would be flexible enough to extract a large number of organic contaminants from a wide range of solid matrices (soil, sand, gravel, sludge, stones, etc.)

APPROACH

The Extraksol™ process was developed through 5 distinct steps;

1 -Laboratory-scale tests were conducted to develop the process's chemistry and better understand the kinetics of the extraction.

2 -These were followed by pilot-scale tests conducted on PCB-contaminated soil. These tests validated the results obtained in the smaller scale but also helped to better define the range of application of the process as well as the most desirable operating parameters. The influence of the matrix on the extraction efficiency was also evaluated.

3 -A one ton per hour Extraksol™ unit was constucted from the conclusions derived in the pilot scale tests. The unit was constructed by ChemVac, a sister company, part of the Sanivan Group.

4 -A series of tests and demonstrations were conducted on the unit's capability to decontaminate PCB containing soil. Troubleshooting of the unit and process upgrading was also performed during this period.

5 -After having demonstrated the unit's capacity to extract PCBs from soil, tests were done to establish the application range and limits of the system. A series of demonstrations were conducted to evaluate the capacity of Extraksol™ to extract a variety of contaminants from different matrices.

Description of the pilot-scale work

1) Objectives

a) establish Extraksol's operating parameters; type of solvent, type of soil that can that can be treated, type of mixing required and appropriate number of extraction cycles;

b) verify the efficiency of the process to extract low concentrations of PCBs from soil heavily contaminated with oils and greases;

c) effect of contact time between the extraction fluid and the soil;

d) effect of different solvent ratios on treatment efficiency.

2) Description of the tests

a) 5 liters of homogenized soil were mixed for 10 min at 30 rpm with 15 liters of the extraction fluid. Mixing was carried within a cement-mixer;

b) After agitation, both liquid and solid phases were transferred into a settling chamber. After separation of both phases, solvent and soil samples were taken for analysis. The solvent was discarded and the soil transferred to the cement-mixer for a second extraction cycle;

c) Steps a and b were repeated as required. The number of extraction cycles applied on each sample was computed. After each extraction cycle the soil and solvent were analyzed for PCBs and oils & greases.

d) After extraction, 0.5 L of the treated soil were weighed and transferred into a sealed, 2 L neck glass bottle. Evaporation of the solvent was carried at a vacuum equivalent to 20 inches of mercury while rotating the flask at 10 rpm on a rotary evaporator.

Description of the full-scale work

1) Process description

A schematic diagram of the one ton per hour Extraksol™ unit is presented in Figure 1, whereas the process's flow sheets are presented in Figures 2 and 3.

The process consists of the following phases:

SOIL WASHING

After introducing 8 or 10 drums of soil (or other contaminated solid material) within the extraction vessel, the extractor is purged and the washing cycle is initiated.

During the soil washing phase, clean solvent is continuously pumped and withdrawn into and from the extractor, creating a dynamic system (Figure 2). To further enhance soil-solvent contact, the extractor is slowly rotated on its axis. At later stages of treatment, used solvent is recycled.

The circulating fluid migrates through the soil and dissolves/desorbs the contaminants present in the matrix according to the affinity of the solvent for the contaminant. The contaminant is transferred from the soil matrix to the solvent and is carried out of the extractor with the fluid. The used solvent is transferred to a storage tank.

The extraction phase is continued until the soil is thought to be decontaminated. Visual analysis of the solvent sampled at the extractor's outlet provides an indication of the state of decontamination. The washing time varies from 1 hour to 2 hours depending on the type and concentration of contaminant within the soil to be decontaminated.

After the soil washing cycles are terminated, the solvent is withdrawn from the extractor and transferred to the contaminated solvent tank.

SOLVENT REGENERATION PHASE

Solvent regeneration is conducted in parallel to the soil washing phase. Regeneration is carried by distillation and takes advantage of the differences in evaporation temperatures of the extraction fluids and the contaminants. The contaminants are concentrated and recovered as residues of distillation.

The solvent regeneration phase is an integral part of the Extraksol™ process which considerably reduces the cost of decontamination. Since the solvent is regenerated to its original composition, it can be reused without limitation and without the need of additives.

SOIL DRYING PHASE

After treatment with Extraksol™, the soil is dry and can often be relocated in its original location.

Soil drying consists of removing the residual solvent from the soil in a closed system operation (Figure 3) .

The drying phase extends from 1 hour to 1 1/2 hours depending on the type of matrix to be treated.

2) Description of the treatments

The demonstrations were conducted according to Extraksol's operational procedures. Further details on the demonstrations are presented in the result tables (Tables 2 to 5).

PROBLEMS ENCOUNTERED

Extraksol™ was conceived, designed, constructed and is now being operated by the Sanivan Group. The system is unique and was developed without background information to be used as reference. Troubleshooting of the process was tedious and improvements to the unit had to be carried out in a stepwise fashion as technical problems arouse whilst operating the full-scale unit. Major process improvements have been added to the full-scale unit during the last year, to improve its treatment's efficiency and to widen the types of matrices and contaminants treatable by Extraksol™.

RESULTS

1)Results of the pilot-scale tests

The results generated from the pilot-scale tests described above are presented in Table 1. The conclusions from these tests are the following:

a) Although the equipment and procedures used could not provide optimal extraction conditions, the percentages of removal achieved in most tests were higher than 80% with some results higher than 95%.

b) From the tests, solvent mixture #2 has better removal efficiency for both PCB and O&G than mixtures #1, #3 or #4. Solvents #3 and #4 are efficent for O&G extraction, but do not extract PCBs in a similarly efficient fashion. This improved efficiency may be explained by the decrease in mass transfer resistance induced by the water adsorbed onto the soil particles. The slight polarity of solvent #2 would overcome such a water interference.

c) The PCB concentration in the solvent decreases after each extraction cycle and tends to be asymptiotic after 3 extraction cycles (refer to Figure 4).

d) The data presented show that there is no apparent benefit in increasing the contact period between soil and solvent for more than 10 minutes.

e) The removal of PCB is not hindered by the large concentration of oil and grease in the soil. Also, a good extraction efficiency is obtained even at low PCB concentrations.

f) The extraction efficiency and the mechanisms of extraction appear to be comparable in both clays and sands. The granulometry of these materials could however interfere in a full-scale treatment.

2)Results of the full-scale demonstrations

The results of the full-scale demonstrations are summarized in Tables 2, 3, 4 and 5.

a) PCB extraction

Full-scale tests confirmed the conclusions derived from the pilot tests, ie. solvent mixture #2 is more efficient for both PCB extraction (Table 2) and oil and greases removal (Table 3). Again, the slight polarity of solvent #2 would allow penetration into the water layer with subsequent dissolution/ desorption of adsorbed contaminants. This mechanism becomes important when decontaminating surface active soils such as clay or clayey soil.

The differences in efficiencies observed between solvents #1 and #2 for PCB extraction in mixed soil was confirmed by the concentration of contaminant within the solvents with time (Figure 5). Figure 5, also shows that the rate of contaminant removal is considerably reduced as the contaminant concentration in the soil is reduced.

This behaviour could be accounted for slower diffusion rates induced by lower concentration differentials between the soil and solvent, which indicates that an equilibrium between the soil and solvent has been reached. Furthermore, after the free contaminants have been flushed with the solvent, different extraction mechanisms become responsible for soil decontamination. Extraction of adsorbed or complexed contaminants involves slower mechanisms where partition coefficients and contaminant affinities become the driving force for soil decontamination.

b) Oils and Greases Extraction

i) Mixed soil
The first 3 results presented in Table 3 refer to mixed soil contaminated with both PCBs and transformer oils. Extraction of the two contaminant sources was done simultaneously. Both PCB and O&G extraction performance were good with solvent #2, with removal rates greater than 90%.

ii) Refinery sludge and soil
The Extraksol™ process was shown to be very efficient to extract hydrocarbons from clayey soil and sludge originating from refinery sites. These materials are often oily and sticky with O&G concentrations exceeding 5% (50,000 ppm). The system has the capacity to declassify the sludge but also to have the treated sludge be relocalized as "soil". After removal of the contaminants, the sludge is a dry, powdery material which can not be distinguished from the refinery's clayey soil.

Extraksol™ is a batch process which offers the flexibilty to treat different types of materials with a large range of granulometries and fabrics. The batch operation also provides a large flexibility of operation; no process adjustement is needed to select the number of extraction cycles required for a particular waste to reach a specific residual contaminant concentration.

For example, the residual O&G concentration aimed when treating the refinery sludge was of 5,000 ppm (Table 3). If required, the sludge could have been further treated, but the costs of decontamination would be raised with increasing number of extraction cycles.

iii) Fuller's earth
Extraksol™ has succesfully decontaminated and regenerated more than 30 tons of Fuller's earth. This diatomic earth is currently used as absorbant and filtration media to purify oils. After use, the Fuller's earth are very oily with O&G concentrations exceeding 30%. Removal efficiencies achieved were in the order of 99% after 2 hours of washing.

iv) Porous gravel and stones
Extraction of hydrocarbons from porous materials is feasible with Extraksol™, but the removal efficiency is lower than with non-porous materials. The surface area of the contaminated matrix appears to interfere with solvent extraction.

With removal percentages ranging from 60% to 80%, solvent circulation does not appear to be the most efficient treatment for porous materials. It is believed that contaminants' extraction could have been improved if the gravel would have soaked in the solvent for a given time, before initiating solvent circulation.

c) PAH extraction
Extraksol™ was shown to be an efficient solution to decontaminate soil and sludge bearing polyaromatic hydrocarbons (PAH). With extraction efficiencies ranging between 80% and 95% and residual PAH concentrations as low as 10 ppm (Table 4), the process offers an acceptable solution for emerging PAH problems.

d) PCP extraction
Extraksol™ has the capacity to extract a large number of chlorinated and non-chlorinated organic contaminants from unconsolidated solids. Although many contaminants such as pesticides, dioxins and furans remain to be tested, treatment of pentachlorophenols (PCP) by Extraksol™ was a success. Even porous gravel which has a tendency to be difficult to treat for oils (refer to Table 3), was decontaminated to non-detectable levels of PCP.

Treatment of activated carbons have shown that these surface active materials have a tendency to be more difficult to decontaminate. Nevertheless, an extraction efficiency equivalent to 89% was obtained with solvent #2 (Table 5). After treatment, the activated carbons retained their physical characteristic and could be re-used as a pre-treatment carbon. Regeneration of carbons by solvent washing is therefore possible with Extraksol™, reducing the cost of disposal and of new material replacement.

CONCLUSIONS

Enough work has been done with the one ton per hour Extraksol™ unit to confirm that the process can effectively extract oils, PCB, PAH, and PCP from soil and generate a "clean", dry soil, which once mixed with top-soil for revegetation can be returned to its original location.

Decontamination of sand, mixed soils clayey soil, sludge, gravel, activated carbon and stones have demonstrated that the process is very flexible and can be adapted to solve a range of environmental problems.

The flexibility and mobility of the 1 ton/hour unit and its 3 day set-up period makes is a perfect process to be used on small projects with a maximum of 300 tons of material to be treated.

The Sanivan Group is planning to build a larger Extraksol unit which will have the capacity to treat 6 to 8 tons per hour. This mobile unit will be designed on the same principles of operation as the smaller unit. This larger unit will be operated by 2 operators as the smaller unit.

The cost of treatment with the larger unit will range from $100 to $200 per ton of material to be treated, depending on the type of matrix, the contaminants' concentration and residual contaminant concentrations.

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Figure 1, Schematic of the one ton per hour Extraksol™ unit

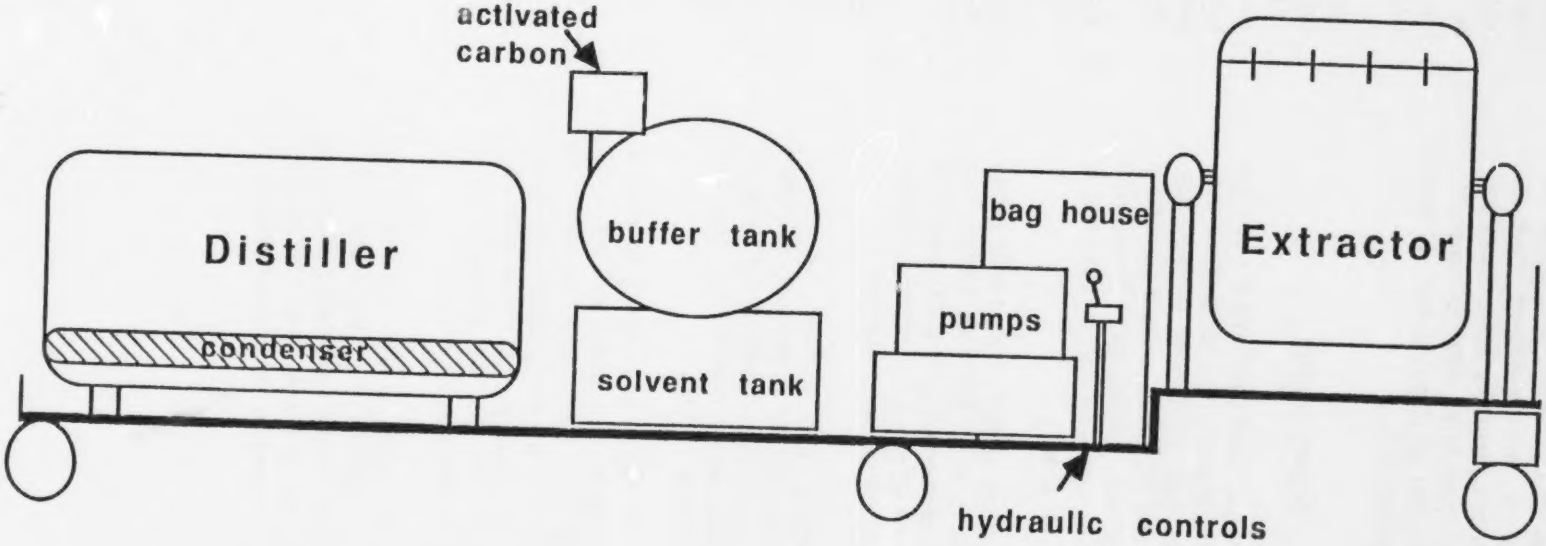
activated
carbon
Distiller
condenser
buffer tank
solvent tank
bag house
pumps
Extractor
hydraulic controls

Figure 2, Schematic of the Extraksol™ Process Extraction Mode

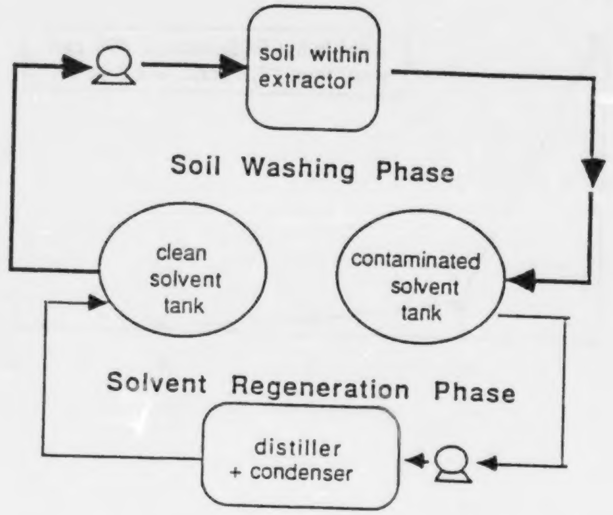
soil within extractor
Soil Washing Phase
clean solvent tank
contaminated solvent tank
Solvent Regeneration Phase
distiller + condenser

Figure 3, Schematic of the Extraksol™ Process Drying Mode

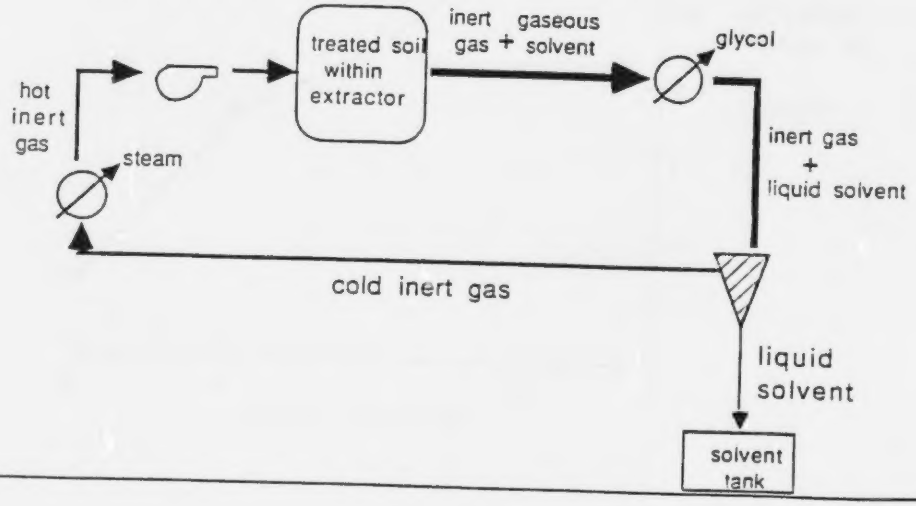
hot inert gas
steam
treated soil within extractor
inert gas + gaseous solvent
glycol
inert gas + liquid solvent
cold inert gas
liquid solvent
solvent tank

FIGURE 4, TYPICAL CONCENTRATIONS OF PCB IN THE SOLVENT
PILOT-SCALE WORK

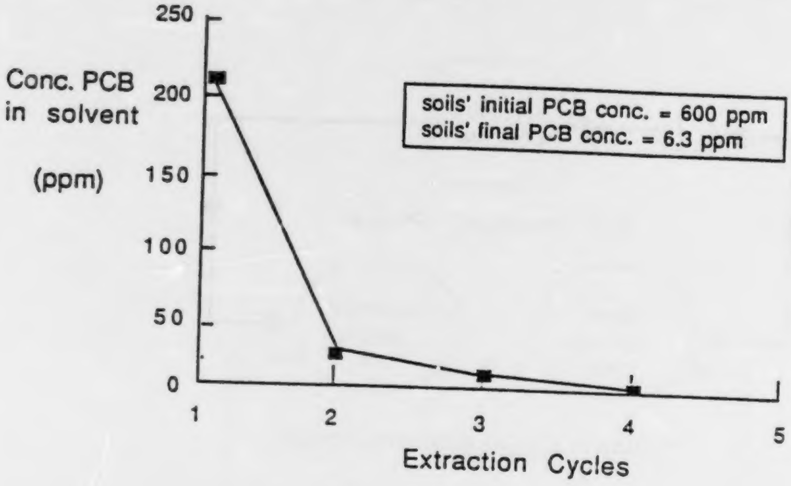

FIGURE 5, TYPICAL CONCENTRATIONS OF PCB IN THE SOLVENT
FULL-SCALE WORK

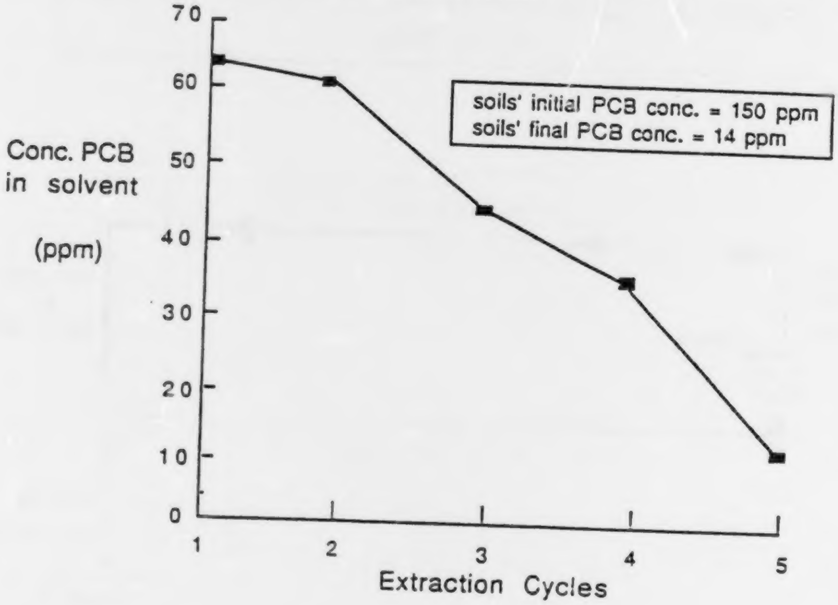

TABLE 1, SUMMARY OF RESULTS OBTAINED WITH EXTRAKSOL'S PILOT SCALE UNIT

TYPE OF SOIL	TYPE OF FLUID	REMOVAL OF OILS AND GREASES			REMOVAL OF PCB		
		Initial Concent. (ppm)	Final Concent. (ppm)	% Removal (%)	Initial Concent. (ppm)	Final Concent. (ppm)	% Removal (%)
Clay	# 1	1,970	847	56.9	7,925	2,080	73.8
Clay	# 2	8,040	590	92.7	2,055	48.8	97.6
Sand	# 1	470	220	53.2	600	6.3	98.9
Mixed Soil	# 1	13,890	2,270	87.7	3.6	0.69	89.0
Mixed Soil	# 2	14,400	1,210	92.0	5.3	0.70	87.0
Mixed Soil	# 3	34,300	1,440	96.0	5.2	1.0	81.0
Mixed Soil	# 4	21,540	1,880	91.0	4.8	1.1	77.0

TABLE 2, SUMMARY OF RESULTS OBTAINED WITH THE 1 TON/HOUR EXTRAKSOL UNIT - PCB REMOVAL

TYPE OF SOIL	TYPE OF FLUID	Initial PCB Concent. (ppm)	Final PCB Concent. (ppm)	% Removal (%)
clay-bearing	# 2	150	14	91.0
clay-bearing	# 1	163	28	82.0
clay-bearing	# 2	54	4.4	92.0

TABLE 3, SUMMARY OF RESULTS OBTAINED WITH THE 1 TON/HOUR EXTRAKSOL UNIT - O&G REMOVAL

TYPE OF SOIL	TYPE OF FLUID	Initial O&G Concent. (ppm)	Final O&G Concent. (ppm)	% Removal (%)
clay-bearing	# 2	1,801	182	90
clay-bearing	# 1	1,789	166	82
clay-bearing	# 2	600	80	92
refinery clayey soil	# 2	15,000	800	95
refinery oily sludge	# 2	49,000	4,200	91
refinery oily sludge	# 2	72,000	2,000	97
refinery oily sludge	# 2	73,000	4,800	93
refinery oily sludge	# 2	70,000	340	99
Fuller's earth	# 2	366,000	4,200	99
Fuller's earth	# 2	447,000	5,500	99
Fuller's earth	# 2	313,000	3,700	99
Fuller's earth	# 2	332,000	4,000	99
pulp & paper porous gravels	# 2	10,000	3,690	63
pulp & paper porous gravels	# 2	1,040	207	80

TABLE 4, SUMMARY OF RESULTS OBTAINED WITH THE 1 TON/HOUR EXTRAKSOL UNIT - PAH REMOVAL

TYPE OF SOIL	TYPE OF FLUID	Initial PAH Concent. (ppm)	Final PAH Concent. (ppm)	% Removal (%)
refinery clayey soil	# 2	332	55	83
refinery oily sludge	# 2	81	16	81
refinery oily sludge	# 2	240	10	96
refinery oily sludge	# 2	150	19	87
refinery oily sludge	# 2	1,739	130	92

TABLE 5, SUMMARY OF RESULTS OBTAINED WITH THE 1 TON/HOUR EXTRAKSOL UNIT - PCP REMOVAL

TYPE OF WASTE	TYPE OF SOLVENT	Initial PCP Concent. (ppm)	Final PCP Concent. (ppm)	% Removal (%)
porous gravel	# 2	8.2	<0.82	>90
porous gravel	# 2	81.4	<0.21	>99.7
porous stones	# 2	38.5	19.5	50
activated carbon	# 2	744	83	89

Disclaimer

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ORGANIC WASTE TREATMENT WITH ORGANICALLY MODIFIED CLAYS

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ABSTRACT

A relatively new technology for the retention and adsorption of organic pollutants involves the use of organically modified clays. The accessible surfaces within the crystalline structure of clay minerals are chemically modified with organic derivatives such as alkylammonium ions. This clay modification imparts an organophilic character to the clay. The clay surface is thus rendered suitable to adsorb organic molecules.

Clays such as bentonite have been used for many years as pond and landfill liners because of their low permeability to water. The low permeability of these clays has been shown to be affected adversely by fluids containing organics. Organically modified clays allow an extension of clay barrier technology into organic systems. As a result of the affinity between organically modified clays and organic pollutants, applications for their use in waste treatment and remediation have evolved. These applications include:

1) Waste stabilization - organically modified clay is mixed with organic wastes and then cementing agents to produce a solidified matrix, resulting in reduced leachability of the organics from the stabilized matrix.

2) Water treatment - organically modified clay is used for treatment of ground and surface water to remove organic constituents within the waste stream.

3) Spill control - organically modified clay can be distributed on water or soil surfaces to sorb organic liquids as necessary for spill control.

4) Tank farm liners - organically modified clay can be used in liner systems for fuel oil storage tanks.

5) Hazardous waste liner systems - organically modified clay can be used as a barrier layer component within liner systems for hazardous waste storage and disposal sites.

INTRODUCTION

The use of organically modified clays in hazardous waste management applications offers a significant new and untapped potential. These clays may be used in the stabilization of organic wastes and organically contaminated soils, for waste water treatment, for oil spill control, for liner systems beneath fuel oil storage tanks, and as a component within liner systems of hazardous waste storage treatment and disposal facilities. Organically modified clays (organophilic clays) may be employed in each of these systems to adsorb organic waste constituents, enhancing the performance of these applications. This paper first describes the nature of organophilic clays, and then discusses their application in each of the five areas.

ORGANICALLY MODIFIED CLAYS

The production of organically modified clays begins with the use of a natural clay mineral. The clay minerals most commonly used in this process are smectites (montmorillonite and hectorite) and attapulgite (palygorskite). Since the structure of each of the base clays differs, the performance of the modified clays will likewise vary. Detailed descriptions of these clays is found elsewhere (6, 11)

Organic Modification of Clays

The investigation of clay-organic interactions began over 50 years ago. An early study reacted organic bases and their salts with montmorillonitic clays and presented evidence that an ion exchange reaction had occurred (6). Similar early experiments using organic chemicals in montmorillonitic clay demonstrated that the exchangeable inorganic cations could be replaced by organic cations, and that uncharged polar compounds could enter the inner layer region without the release of cations (13). It was also found that bentonite, after reaction with certain organic compounds, gains the properties of swelling and dispersing in organic fluids (8). These studies describe the clay-organic interactions which impart the organophilic characteristics upon the modified clay. Since that time, these interactions have proven to be effective and, in many cases, commercially viable in transforming a naturally hydrophilic clay into an organophilic clay.

A number of chemical interactions between the clay and organic compound were identified in the organic modification of clays. The primary reactions which occur are adsorption, intercalation, and cation exchange. Additional reactions include ion exchange, anion exchange, protonation of organic molecules at the clay surface, hemisalt formation, ion-dipole coordination, hydrogen bonding, pi-bonding, entropy effects, and covalent bonding (10). It is beyond the scope of this paper to discuss in detail these reactions, which influence the organic modification of clays.

To produce an organically modified clay, an unmodified clay mineral is reacted with an organic compound. In this process, a cationic surfactant, such as quaternary ammonium, replaces the exchangeable inorganic sodium, calcium and/or magnesium ions on the negatively charged surface of the clay. In this reaction, the clay's nature is converted from a hydrophilic to an organophilic condition. Reaction of the clay with the appropriate organic cation will result in a modified clay which will swell and disperse in the presence of a variety of organic liquids.

The organic compounds most commonly used to modify clays are quaternary ammonium salts. A quaternary ammonium salt is a form of an organic nitrogen compound in which the molecular structure includes a central nitrogen atom joined to four organic groups along with an acid radical. They are all considered cationic, surface active coordination compounds and tend to be adsorbed on surfaces, thus the term surfactants. The most commonly employed types of quaternary ammonium compounds used to modify clays are dimethyl ammonium, methyl benzyl ammonium, dibenzyl methyl ammonium, and benzyl dimethyl ammonium quats.

Manufacture of Organically Modified Clays

Organically modified clays are manufactured using either a dry process or a wet process. In a wet process, the unmodified clay is mixed with water, forming a slurry. The resulting slurry is centrifuged to remove inert, non-clay minerals. The supernatant, which contains ultra-pure clay, is then reacted with the specified organic compound. The mixture is filtered, dried and ground. In the dry process, limited amounts of water are first added to the unmodified clay. The clay is then reacted with the organic compound in a mixer, pug mill or extrusion device. Finally, the reacted material is dried and ground. Since centrifugation is not performed in the dry process, some impurities still exist in the finished clay product. Additional detail regarding the clay manufacture can be found elsewhere (1, 5, 12).

Adsorption by Organophilic Clays

Organically modified clays are suitable media for the adsorption of soluble organic compounds from dilute aqueous solutions. This adsorption occurs through electrostatic/hydrogen bonding forces at the hydrophilic sites, and by van der Waals forces at the organophilic sites of the organophilic clay. The following factors affect the adsorption of organic compounds from dilute aqueous solutions by organophilic clays: a) the nature of the adsorption sites, b) the nature of the organic molecules to be adsorbed, c) spatial considerations, d) thermodynamic quantities, and e) solubility of the adsorbate in the solvent (4). Portions of the organically modified clay surface which were not modified during the organic modification process are still hydrophilic. As a result, adsorption by electrostatic/hydrogen bonding with the hydrophilic portion of the adsorbate molecule occurs at these hydrophilic clay sites. On the remainder of the clay surface, which is organophilic, van der Waals bonding occurs. Since adsorption occurs at both types of sites on the clay surface, a balance between the organophilic and hydrophilic clay sites optimizes the adsorption capacity of the clay (4).

LABORATORY TESTING PROGRAM

The adsorption capacity of a number of commercially available organically modified clays was quantified utilizing the free swell, or sedimentation, test. In each of these tests, 50 milliliters (ml) of the test fluid were poured into a 100-ml graduated cylinder and 2.5 grams of the clay were then rained into the fluid. The clay typically settled to the bottom of the graduated cylinder. The free swell volume was recorded after 24 hours. The laboratory test procedure for this free swell test was modified from laboratory procedures previously developed (7). The major modification from the original procedure was the reduction in the quantity of clay and test fluid utilized. These investigations parallel a study published earlier in which a single organically modified clay type was evaluated (8, 9). This swell volume is only an indicator of the clay's adsorption capacity, and may not adequately quantify the performance of the clay in the applications discussed herein.

The clays and their manufacturers are listed in Table 1 along with pertinent information regarding the manufacture of the organophilic clays. The organic compounds reacted with the base clays are quaternary ammonium salts, primarily dimethyl di(hydrogenated tallow) ammonium chlorides. Tallow is an animal fat with each organic molecule containing 16 to 18 carbon atoms.

Ten test fluids were used in these studies: acetic acid, acetone, aniline, carbon tetrachloride, deionized water, diesel fuel, hexane, kerosene, unleaded gasoline, and xylene. All of the fluids employed in the study were added in a concentrated form with each of the clays studied. The results of the free swell tests conducted for these studies, along with the density of each clay, are summarized in Table 2.

DISCUSSION OF LABORATORY TEST RESULTS

Examination of the average free swell volume enables a comparison between the various organically modified clays for a wide range of organic fluids. Viewing the data in this way, it is revealed that all of the organically modified clays have an average free swell volume between 11 and 35 ml. The wet process clays with the highest average free swell volumes are Baragel 3000 (34.3 ml), Benathix 1-4-1 (32.1 ml) and Tixogel SP (31.6 ml). The dry process clays with the highest average free swell volumes are PC-1 (23.8 ml) and TS-55 (23.1 ml). The two unmodified clays, bentonite and attapulgite, have the lowest average free swell volumes, indicating they did not swell appreciably in the presence of the concentrated organic test fluids.

In summary, it is believed that these tests provide a useful way to rapidly and quantitatively compare the expected performance of organically modified clays. Note that clay cost must be evaluated in comparison to performance in selecting a particular clay for a particular application.

APPLICATIONS

With the ability of the organically modified clays to adsorb organics, a number of applications for organically modified clays in pollution control and hazardous waste site remediation have been identified. These applications range from those fully developed and in the marketplace to those recently proposed. The following section discusses several applications for organically modified clays.

Waste Stabilization

The remediation of organically contaminated soils and wastes employing stabilization and solidification techniques has become increasingly widespread. The stabilization process is designed to maximize shear strength and minimize the rate of leaching of hazardous constituents from the stabilized matrix into the environment. Conventional stabilization techniques, such as cement and flyash, are usually limited to inorganic, metal-bearing wastes. For organic wastes, modified clays have been employed to adsorb organic constituents. Preliminary laboratory data indicate that organophilic clays are effective as stabilization agents (12).

When used in conjunction with conventional cement-based or pozzolanic additives, organically modified clays are effective in reducing the mobility of organic constituents from the stabilized matrix. Reductions in the mobility of organics has been demonstrated and is the subject of several patents (2, 3). Organically modified clays are first mixed with the waste to adsorb the organic constituents. In this manner, the organics are chemically bound within the organoclay, thereby reducing the organic interference with the normal cement reactions and lattice formation. The clay, with organic contaminants bound within the clay structure, is then macroencapsulated in a cementitious matrix formed by a cement or pozzolan. This technique, which utilizes an organophilic clay in conjunction with a cement product, is employed by the Silicate Technology Corporation of Scottsdale, Arizona for the stabilization of organic hazardous wastes. In this technique, the leaching potential of the organic constituents is decreased through the use of organophilic clays as compared to techniques using only cement or pozzolan in the stabilization process.

Water Treatment

Organically modified clays are used to treat organically contaminated waste water. In this process, the aqueous solution is filtered through organically modified clay and the organic contaminants are adsorbed by the clay. Unlike activated carbon, which adsorbs organic contaminants through surface related phenomena, organically modified clays swell as the organic contaminants are sorbed into the clay structure. Thus, the organic molecules of the contaminant preferably partition into the organic phase of the organoclay instead of the aqueous phase

(2). Volatile organics are poorly adsorbed, whereas oils and greases are readily adsorbed as a result of their differing partition coefficients.

Organically modified clays are typically used along with other water treatment technologies. For example, when used in a treatment system upstream of activated carbon, the carbon life is greatly extended as a result of the removal of high molecular weight organics. Two commercially available products, Calgon's Klensorb 100TM and Electrum's Organosorb, contain an organically modified clay to remove organics from a waste stream. The organophilic clay in these products is used with an anthracite filter media to provide an effective column filtration medium in water and waste water treatment. The combination of this mixed media and granular activated carbon adsorption facilitates the removal of a broad range of both soluble and insoluble compounds. Shown on Figure 1, are the influent and effluent oil concentrations for an oily steam condensate filtered with a mixture of Organosorb and anthracite filter media. The treatment effectiveness is demonstrated on Figure 1 and an annual savings of about $150,000 per year was projected for a 500 to 600 gpm system 14). In another application, the organically modified clay removes non-volatiles prior to air stripping, thereby increasing the efficiency of the system.

Spill Control

The organophilic nature of organically modified clays make them suited for use in spill control applications. As demonstrated in the laboratory studies, these clays will either float on or sink to the bottom of an aqueous solution, depending on the nature of the organic modification. For example, an oil spill on water can be sorbed by the organoclay and held within the clay crystalline structure for cleanup and disposal. For a spill where the materials sink, the clays could likewise be selected to sink through the water and sorb the spilled fluid.

Tank Liners

Fuel oil storage tanks are typically surrounded with a liner and berm system to contain the fuel oil should a leak occur. As a result of the impervious nature of the liners used in these systems, they also contain precipitation. As an alternative to conventional liner systems, it is proposed that organically modified clays be used. An organically modified clay liner would permit precipitation to flow downward through the liner without accumulating in the containment system. In the event of a tank leak, the clay will swell in the presence of the fuel and form an impervious barrier layer. This would prevent migration of contaminants into the subsurface. It may also be possible to use organically modified clays as secondary containment barriers beneath/around underground storage tanks in a similar manner.

Landfill Liners

The technology for landfill liners has been evolving in recent years to include multimedia barrier layers to optimize the environmental protection. Presently, liner systems include both geomembrane barrier layers and natural clay barriers. The greatest environmental concern at present is that both geomembranes and natural clays may be subject to degradation in the presence of organic contaminants. Further, organic contaminants may migrate through these materials in response to chemical diffusion gradients. It is proposed that the liner system include a barrier layer composed of an organically modified clay. In this way, the multimedia liner system would have superior performance in the presence of organic contaminants. The sorptive capacity of these materials would significantly reduce the rate of organic contaminant transport across the liner system.

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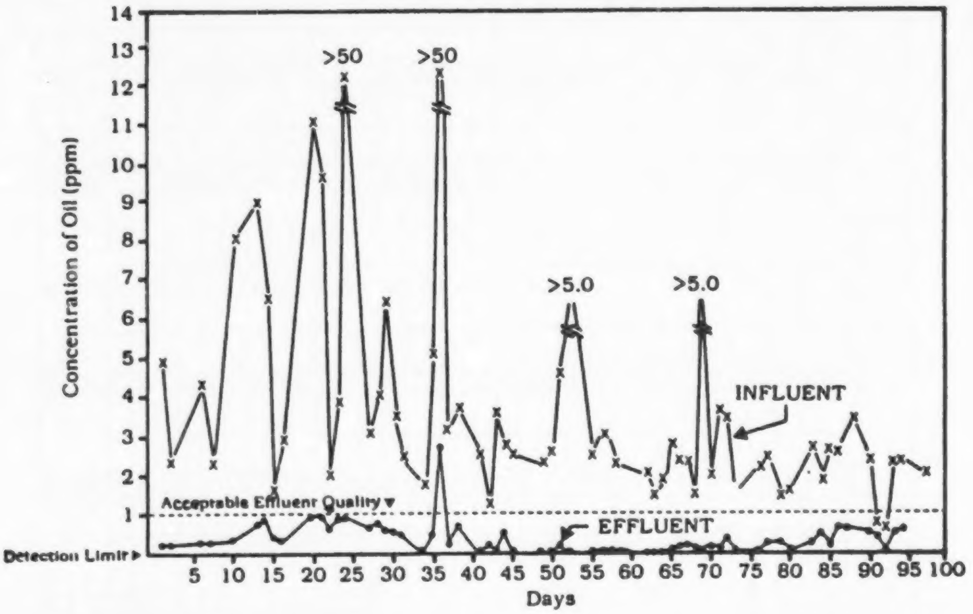

Figure 1. Influent and Effluent Concentrations (from Electrum, Inc.)

Table 1. Summary of Clay Information

CLAY	BULK DENSITY (g/cm3)	DEIONIZED WATER (ml)	ACETIC ACID (ml)	ACETONE (ml)	ANILINE (ml)	CARBON TETRA-CHLORIDE (ml)	HEXANE (ml)	KEROSENE (ml)	XYLENE (ml)	DIESEL FUEL (ml)	UNLEADED GASOLINE (ml)	AVERAGE (ml)
Attapulgite	0.52	15.5	7.0	6.5	8.0	6.0	7.0	7.0	7.0	7.0	6.0	6.8
Bentonite	0.78	34.0	4.5	6.0	4.5	5.0	5.0	5.0	5.0	4.0	4.0	4.8
Attatone J	0.25	16.0	8.0	19.0	14.5	23.0	15.0	17.5	26.0	25.0	20.0	18.7
Attatone T	0.58	8.5	13.0	20.0	7.0	11.0	8.0	8.5	12.0	11.0	11.5	11.3
BC 90	0.40	8.5	11.0	11.5	7.5	7.0	18.0	18.0	20.0	20.0	29.0	15.8
Bondtone	0.53	7.0	8.0	13.0	7.5	0.0	40.0	20.0	36.0	19.0	21.0	18.3
Claytone APA	0.24	14.0	19.0	17.5	23.0	0.0	9.0	21.0	50.0	36.0	36.0	23.5
Claytone 40	0.47	0.0	13.0	14.0	12.0	0.0	12.0	22.0	48.0	46.0	29.5	21.8
2HT	0.52	6.0	8.0	11.0	8.0	15.0	47.0	27.0	43.0	20.0	18.0	21.9
2HT Aberdeen	0.51	10.0	10.0	16.0	8.5	3.0	12.0	18.0	18.0	20.0	27.0	14.7
P-1	0.36	9.0	12.0	13.5	11.0	0.0	13.0	18.0	27.0	21.0	22.5	15.3
P-11	0.34	8.0	9.0	10.0	9.0	25.0	25.0	22.0	25.0	18.0	20.0	18.1
P-40	0.51	7.0	9.0	13.0	8.0	33.0	13.0	26.0	20.0	16.0	31.0	18.8
PC-1	0.39	8.0	8.0	26.0	8.0	20.0	45.0	33.0	24.0	25.0	25.0	23.8
PT-1	0.44	7.0	9.0	22.0	8.0	10.0	15.0	32.0	22.0	28.0	29.0	19.4
Suspentone	0.50	10.0	11.0	15.0	9.0	6.0	28.0	35.0	33.0	17.0	28.0	20.2
TS-55	0.41	6.0	7.0	8.0	7.0	40.0	34.0	24.0	28.0	21.0	39.0	23.1
Tixogel DS	0.42	7.0	12.0	13.5	12.0	30.0	26.0	25.0	51.0	25.0	25.0	24.4
Tixogel EZ-100	0.49	6.0	11.0	12.0	11.0	20.0	47.0	30.0	20.0	20.0	15.0	20.7
Tixogel GB	0.53	7.0	9.0	11.0	8.5	0.0	13.5	24.0	20.0	20.0	13.0	13.2
Tixogel PE	0.44	7.0	11.0	20.0	16.0	0.0	10.0	15.0	25.0	20.0	35.0	16.9
Tixogel SP	0.43	11.0	14.0	15.0	13.5	25.0	18.0	49.0	50.0	50.0	50.0	31.6
Tixogel TE	0.42	8.0	13.0	16.0	13.0	0.0	16.0	37.0	51.0	50.0	50.0	27.3
Tixogel VP	0.50	10.0	12.0	15.0	12.0	28.0	10.0	19.0	20.0	49.0	35.0	22.2
Tixogel VZ	0.28	10.0	12.0	32.0	19.0	13.0	9.0	11.0	25.0	21.0	13.0	17.2
Bentone 27	0.55	8.0	12.0	14.5	16.0	7.0	5.0	6.0	22.0	12.0	8.0	11.4
Bentone 34	0.55	13.0	15.0	14.0	12.0	0.0	10.0	28.0	22.0	48.0	34.0	20.3
Bentone 38	0.46	15.0	18.0	15.0	14.0	43.0	9.0	18.0	39.0	32.0	10.0	22.0
Baragel 3000	0.43	16.0	16.0	20.0	14.0	30.0	42.5	36.0	50.0	50.0	50.0	34.3
Bentone SD-1	0.36	0.0	13.0	14.0	16.0	32.0	40.0	25.0	50.0	35.0	40.0	29.4
Bentone SD-2	0.37	14.0	14.0	30.0	24.5	32.0	8.0	9.0	52.0	32.0	20.0	24.6
Bentone SD-3	0.56	0.0	13.5	13.0	12.0	45.0	14.0	30.0	32.0	49.0	37.0	27.3
Benathix 1-4-1	0.25	18.0	36.0	39.0	27.0	14.0	11.0	13.0	52.0	49.0	48.0	32.1

Table 2. Laboratory Test Results

CLAY	MANUFACTURER	PROCESS	BASE CLAY	ORGANIC MODIFIER
Attapulgite	Engelhard Specialty Chemicals	None	Attapulgite	None
Bentonite	NL Baroid	None	Bentonite	None
Attatone J	Bentec	Dry	Attapulgite	Dimethyl di(hydrogenated tallow) ammonium chloride
Attatone T	Bentec	Dry	Attapulgite	Dimethyl di(hydrogenated tallow) ammonium chloride
BC 90	Bentec	Dry	Hectorite	Dimethyl di(hydrogenated tallow) ammonium chloride
Bondtone	NL Baroid	Dry	Bentonite	Methyl benzyl di(hydrogenated tallow) ammonium quat
Claytone APA	Southern Clay Products	Wet	Bentonite	Proprietary amine
Claytone 40	Southern Clay Products	Wet	Bentonite	Dimethyl di(hydrogenated tallow) ammonium quat
2HT	NL Baroid	Dry	Bentonite	Methyl benzyl di(hydrogenated tallow) ammonium quat
2HT Aberdeen	Bentec	Dry	Ca Bentonite	Dimethyl di(hydrogenated tallow) ammonium chloride
P-1	Bentec	Dry	Bentonite	Dimethyl di(hydrogenated tallow) ammonium chloride
P-11	Bentec	Dry	Bentonite	Dimethyl di(hydrogenated tallow) ammonium chloride
P-40	Silicate Technology Corp.	Dry	Bentonite	Dimethyl di(hydrogenated tallow) ammonium quat
PC-1	Bentec	Dry	Bentonite	Dimethyl di(hydrogenated tallow) ammonium chloride
PT-1	Bentec	Dry	Bentonite	Dimethyl di(hydrogenated tallow) ammonium chloride
Suspentone	NL Baroid	Dry	Attapulgite	Dimethyl di(hydrogenated tallow) ammonium quat
TS-55	NL Baroid	Dry	Bentonite	Methyl benzyl di(hydrogenated tallow) ammonium quat w/ polymer (elastomer)
Tixogel DS	United Catalyst	Wet	Bentonite	Methyl benzyl di(hydrogenated tallow) ammonium chloride
Tixogel EZ-100	United Catalyst	Wet	Bentonite	Dimethyl di(hydrogenated tallow) ammonium chloride
Tixogel GB	United Catalyst	Wet/Dry	Bentonite	Dimethyl di(hydrogenated tallow) ammonium chloride
Tixogel PE	United Catalyst	Wet	Bentonite	Methyl benzyl di(hydrogenated tallow) ammonium chloride
Tixogel SP	United Catalyst	Wet	Bentonite	Methyl benzyl di(hydrogenated tallow) ammonium chloride
Tixogel TE	United Catalyst	Wet	Bentonite	Dimethyl di(hydrogenated tallow) ammonium chloride
Tixogel VP	United Catalyst	Wet	Bentonite	Dimethyl di(hydrogenated tallow) ammonium chloride
Tixogel VZ	United Catalyst	Wet	Bentonite	Methyl benzyl di(hydrogenated tallow) ammonium chloride
Bentone 27	NL Chemicals	Wet	Hectorite	Methyl benzyl di(hydrogenated tallow) quat
Bentone 34	NL Chemicals	Wet	Bentonite	Dimethyl di(hydrogenated tallow) quat
Bentone 38	NL Chemicals	Wet	Hectorite	Dimethyl di(hydrogenated tallow) quat
Baragel 3000	NL Chemicals	Wet	Bentonite	Dimethyl di(hydrogenated tallow) quat
Bentone SD-1	NL Chemicals	Wet	Bentonite	Methyl benzyl di(hydrogenated tallow) quat
Bentone SD-2	NL Chemicals	Wet	Bentonite	Dimethyl benzyl (hydrogenated tallow) quat
Bentone SD-3	NL Chemicals	Wet	Hectorite	Methyl benzyl di(hydrogenated tallow) quat
Benathix 1-4-1	NL Chemicals	Wet	Bentonite	Dimethyl benzyl (hydrogenated tallow) quat

Disclaimer

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TECHNOLOGIES APPLICABLE FOR THE REMEDIATION OF CONTAMINATED SOIL AT SUPERFUND RADIATION SITES

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ABSTRACT

This paper identifies technologies that may be useful in removing or stabilizing radioactive contamination at Superfund hazardous waste sites containing radioactive material. The radioactive materials at some of these sites consist primarily of waste from radium, uranium, and thorium processing. Twenty-five existing Superfund sites are known to contain radionuclides.

Sites contaminated with radioactive material pose a unique problem because, unlike organic wastes, radioactive contaminants cannot be destroyed by physical or chemical means; they can only decay at their natural rate. Alteration of the radioactive decay process thereby changing the fundamental hazard is not possible. Several technologies have potential for removing or stabilizing radioactive material at Superfund sites. These fall into the categories of disposal, on-site treatment, chemical extraction, physical separation, and soil washing. Applicability of these technologies is controlled by site-specific factors, and their feasibility must be determined on this basis.

INTRODUCTION

The United States Environmental Protection Agency (USEPA) has identified 25 Superfund sites in the country that are radioactively contaminated. They are listed in Table 1. The radioactive materials at many Superfund sites are by-products of uranium, thorium, and radium processing in the form of tailings, contaminated buildings

TABLE 1. SUPERFUND SITES CONTAINING RADIOACTIVE CONTAMINANTS

Site Name	City/County	State/EPA Region	Acres	Cu yds
1. Shpack/ALI	Norton/Attleboro	MA/I	31	--
2. Maywood Chemical Co./ Sears Property	Maywood/Bergen Co.	NJ/II	42	270,000
3. U.S. Radium Corp.	Orange, Essex Co.	NJ/II	1	10,000
4. W. R. Grace & Co.	Wayne/Passaic Co.	NJ/II	6.5	120,000
5. Montclair, West Orange,	Essex Co.	NJ/II		
6. Glen Ridge Radium Site	Essex Co.	NJ/II	127.0	350,000
7. Lodi Municipal Well	Lodi, Bergen Co.	NJ/II	wells	--
8. Lansdowne Property	Lansdowne	PA/III	1.9	2,000
9. Maxey Flats Nuclear Disposal Site	Fleming City/Hillsboro	KY/IV	25.0	178,000
10. West Chicago Sewage Treatment Plant	West Chicago	IL/V	25.0	40,000
11. Reed-Keppler Park	West Chicago	IL/V	0.25	20,000
12. Kerr-McGee Off-Site Properties	West Chicago	IL/V	--	61,000
13. Kerr-McGee Kress Creek/ West Branch of Dupage River	West Chicago	IL/V	--	--
14. The Homestake Mining Co.	Cibola Co.	NM/VI	245	16,500,000
15. United Nuclear Corp.	Church Rock	NM/VI	170	4,700,000
16. Weldon Spring Quarry	St. Charles City	MO/VII	220	780,000
17. Monticello Radioactivity-Contaminated Properties	Monticello San Juan, Co.	UT/VIII	--	182,000
18. Denver Radium Superfund Sites	Denver	CO/VIII	40	106,000
19. Lincoln Park	Canon City	CO/VIII	900	1,900,000
20. U.S. DOE Rocky Flats Plant	Golden	CO/VIII	6,550	--
21. Uravan Uranium Project	Montrose City/Uravan	CO/VIII	900	10,000,000
22. Teledyne Wah Chang	Albany	OR/X	--	--
23. Hanford 200-area (USDOE)	Benton, CO	WA/X	--	1,000,000,000
24. Hanford 300-area (USDOE)	Benton, CO	WA/X	--	27,000,000
25. Hanford 100-area (USDOE)	Benton, CO	WA/X	--	4,300,000,000

and equipment, and stream sediments. These sites, located across the United States, vary greatly in size and may involve radiation exposure to people who reside on and around them.

These sites if not remediated pose a potential threat to human life and the environment. Possible effects on human health include the increased risk of cancer and increased risk of genetic damage that may cause inheritable defects in future generations.

PURPOSE

Sites contaminated with radioactive material pose a unique problem because unlike organic waste, radioactive materials cannot be destroyed by physical or chemical means; they only decay at their natural rate. The purpose of this paper is to review potential soil remediation technologies that can reduce the mobility or volume of the contaminated material, such that treatability studies for remediation of these sites can be identified.

APPROACH

Technologies that have potential to remediate structures (buildings) and groundwater are of interest at some Superfund radiation sites, but these are beyond the scope of this paper. The soil remediation technologies discussed in this paper fall into the categories of disposal, on-site treatment, chemical extraction, physical separation, and soil washing. Applicability of these technologies to Superfund radiation sites is controlled by site-specific factors; therefore, their usefulness must be determined on a site-by-site basis.

On-Site Disposal: Capping

This concept involves covering the contaminated site with a barrier sufficiently thick and impermeable to minimize the diffusion of radon gas (1). Barrier materials can be either natural low-permeability soils (e.g., clay) or synthetic membrane liners, or both.

- Application: Appropriate for large discrete contaminated areas, or several smaller areas that are close together.
- Advantages: Low cost, easily applied, well-known, and a proven technology.
- Limitation: Limits further use of the site. The cap must be maintained as long as the contaminant exists at the site. Also, horizontal migration of the radioactive material in groundwater could still occur.
- Experiences: Exists for radioactive contaminated soils and tailings (1,2).
- Cost: $13-200 per m^3(3). Low cost for cap only, high cost for excavation, transportation, legal assistance, and cap.

On-Site Disposal: Vertical Barrier Walls

Vertical barrier walls may be installed around the contaminated zone to help confine the material and any contaminated groundwater that might otherwise flow from the site. The barrier walls, which might be in the form of slurry walls or grout curtains (4), would have to reach down to an impermeable natural horizontal barrier, such as a clay zone, in order to be effective in impeding groundwater flow.

- Application: Could be considered for large discrete waste material or around several smaller areas that are close together.
- Advantages: Simple to install, and applicable to a variety of soil conditions.
- Limitation: Restricts further use of the site, possible deterioration of the barrier walls resulting from the chemicals contained in the waste, would not stop vertical contamination to groundwater below.
- Experiences: Exists for hazardous wastes and not for radioactive wastes (4).
- Cost: $33-377 per m^2 of vertical face (4).

Off-Site Disposal: Land Encapsulation

Land encapsulation has been the disposal method most used to this point in time for low-level radioactive waste materials. Land encapsulation can be as simple as excavating the contaminated material and, without further treatment, hauling it to a secure site.

- Application: Appropriate for wastes that have not been treated, as well as for radionuclides extracted from a soil or other type of matrix.
- Advantages: Low cost, proven, workable technology for the disposal of low-level radioactive wastes.
- Limitation: Finding a site is politically and socially difficult. Transportation of large volumes also carries certain costs and risks. Longevity is a consideration not fully addressed by this disposal method.
- Experiences: Exists for radioactively contaminated soils (3).
- Cost: $276-895 per m^3 of contaminated soil (3).

Off-Site Disposal: Land Spreading

This technology involves excavation of the contaminated material, transporting it to a suitable site, and spreading it on unused land, assuring that radioactivity levels approach the natural background level for these materials when the operation is completed.

- Application: Appropriate for dry, granular tailings and soils with very low level radioactivity.
- Advantages: Simple and relatively inexpensive.
- Limitation: Selecting a site is both politically and socially difficult. Also, it could contribute to a non-point source pollution problem.
- Experiences: Very limited.
- Cost: Not available.

Off-Site Disposal: Underground Mine Disposal

Underground mine disposal could provide secure and remote containment for radioactive waste. The radioactive waste could be excavated and transported without treatment to the mine site, pretreated for volume reduction, or solidified to facilitate transport and placement, thus reducing associated costs. Movement of radionuclides into groundwater must be investigated and prevented.

- Application: Appropriate for variety of radionuclides and matrix types.
- Advantages: Would provide a very secure and remote containment.

- Limitation: Expensive. Transportation costs and associated risks need to be researched further.
- Experiences: Very limited (1).
- Cost: \$399-942 m^3 of contaminated soil (1).

Off-Site Disposal: Ocean Disposal

A possible alternative to land-based disposal options is ocean disposal. This alternative should only be considered for tailings and other radioactive soils that are free of other hazardous waste, because of potential danger to marine biota.

- Application: Appropriate for low-level radioactive waste.
- Advantages: Offers extreme isolation of low-level radioactive waste.
- Limitation: Stringent permit requirements.
- Experiences: Exists for radioactive wastes (1).
- Cost: \$332-400 per m^3 of contaminated soil (2).

On-Site Treatment: Stabilization/Solidification

This method immobilizes radionuclides by trapping them in an impervious matrix (4). The solidification agent (i.e., Portland cement, silica grout, or chemical grout) can either be injected in situ, or the waste can be excavated, mixed, and returned.

- Application: Can be applied to buried and/or capped material.
- Advantages: Solidification may be able to reduce the release of radon and associated radioactivity to acceptable levels. Solidification also may make it easier to transport and dispose of the waste material off site.
- Limitation: Long-term effects are not known. There can be undesired reaction between the additives and other types of hazardous waste.
- Experiences: Exists for hazardous wastes and not for radioactive wastes (4).
- Cost: \$44-328 per m^3 of contaminated soil (4).

On-Site Treatment: Vitrification

This technology immobilizes radioactive contaminants by trapping them in an impervious matrix. The in situ process melts the waste materials between two or more electrodes, using a large amount of electricity. The melted material then cools to a glassy mass in which the radionuclides are trapped.

- Application: Applicable for low-level radioactive wastes.
- Advantages: Minimal site preparation required.
- Limitation: Many substances volatilize, requiring gas collection system. Radium may volatilize, therefore extra precautions are required.
- Experiences: Limited (1).
- Cost: \$161-600 per m^3 of contaminated soil (3).

Chemical Extraction

The various applicable chemical extraction techniques include extraction with inorganic salts, mineral acids, and complexing agents.

Radioactive contaminants can be extracted by thoroughly mixing soil and mill tailings with different chemical solutions. The clean coarse solids are separated from the extractant solution by physical methods. The radioactive material is removed from the extractant solution by ion exchange, coprecipitation, or membrane filtration.

- Application: Various applications depending on reagents used.
- Advantages: High percentage of radium, thorium, and uranium removal possible depending on reagents used.
- Limitation: The resulting chemically leached material may create a harmful waste stream. Reagents can be expensive and may require corrosion resistant materials.
- Experiences: Limited laboratory- and bench-scale testing. Some extraction of radioactive material from ores. (1,5-10)
- Cost: \$66-199 per m^3 of contaminated soil.

Physical Separation

The radioactive contaminants in soils and tailings in many cases are associated with the finer fractions (1,11). Thus, size separation may be used to reduce the volume of concentrated material for disposal, leaving a cleaner fraction. Physical separation may be used with extraction to further reduce contaminant volume. Four physical separation technologies that can be used are screening, both wet and dry; classification; flotation; and gravity concentration. (12-14)

- Application: Applicable for a variety of soils depending on method used.
- Advantages: Can be simple and inexpensive method.
- Limitation: Some soils may be hard to separate. Some methods have low capacity.
- Experiences: Mature technologies with extensive use in industry and ore processing.
- Cost: Equipment costs for four technologies are:
  - Screening--\$4.4-11 per Kg/hr capacity
  - Classification--\$.22-1.1 per Kg/h capacity
  - Flotation--\$10-52 per L/s capacity
  - Gravity Concentration--\$4.1-4.73 per L/s capacity

Soil Washing

Soil washing uses a combination of physical separation and chemical extraction technologies. Contaminated soil or tailings are mixed with water and/or extraction reagents. The clean coarse particle sizes are separated from the liquid containing the fines and radioactive material by a combination of physical separation methods. The radioactive material would then be extracted from the liquid by standard water treatment processes such as filtration, carbon treatment, ion exchange, chemical treatment, and membrane separation.

- Application: Depends on chemical reagents used.
- Advantages: High percentage of contaminant removal is possible. Recycling of reagents is possible.
- Limitation: Expensive reagents. Chemically leached material may create a harmful waste stream.
- Experiences: Only laboratory- and bench-scale testing (1).
- Cost: \$66-132 per m^3 of contaminated soil.

RESULTS

- The 25 Superfund sites have radiologically contaminated soil spread over a total of 9,500 acres and have several contaminated groundwater wells.

- Alteration of the radioactive decay process thus changing the fundamental hazard is not possible.

- Any choice of remediation technologies for radioactive waste at Superfund sites is site specific. Extensive site soil characterization studies would be required prior to development and application of most of the technologies.

- Since none of the chemical extraction and physical separation technologies have been used in a radioactive site remediation situation, their application must be approached cautiously. The same holds true for solidification and stabilization processes. Historically, only land encapsulation has been used to remediate similar sites; ocean disposal has been used for low-level radioactive wastes.

- Various remediation technologies have potential to reduce the volume of the contaminated waste with an associated increase in concentration of the radioactive material.

- Every site remediation involving radioactive materials must involve a final environmentally safe disposal site for the radioactive materials.

- Even if it proves feasible at a particular site to lower the concentration to some acceptable level of radionuclides in the soil by physical separation and/or chemical extraction, the "clean" fraction is likely to contain traces of radionuclides. Therefore, adequate attention must be given to whether the "clean" fraction may be returned to the original site or an unrestricted location or must be sent to a disposal site.

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

Advanced Technologies for Pollutant Detection, Monitoring, and Remediation in Ground Water

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Abstract

Advances in technology for detection, monitoring, and remediation of hazardous waste constituents both in soil and ground water are rapidly changing. Conventional drilling and sampling for pollutant detection is giving way to sophisticated in situ technologies. One of the most promising is the use of cone penetration testing. The cone penetration test has been useful in the siting of waste disposal facilities and in the design of remedial action alternatives. Various types of cone penetrometers have been used to conduct a number of in situ tests where accurate information on soil stratigraphy and variability is essential for the consideration and evaluation of various hazardous waste disposal technologies.

Introduction

During site investigations, the owner/operator is interested in obtaining data toward the ultimate goal of ground water remediation. The data of primary concern are the vertical and lateral extent of the contaminants and their respective concentrations, as well as subsurface geological data. Conventional sources available for the gathering of this data include soil borings, installation of monitoring wells, geophysical methods, and aquifer testing.

One method of collecting site data is the cone penetrometer test (CPT). This method can be used to define such factors as sand geometry, hydraulic conductivities, detailed stratigraphy, and other soil properties. Once these data are collected, the remediation options can be examined to determine which is best suited for the project at hand.

Equipment and test procedures

The cone penetration test involves pushing a cone-shaped instrument into the soil and measuring its resistance to penetration. The two basic types of instruments are mechanical and electrical cone penetrometers.

The electronic cone penetrometer is shown in Figure 1. As it penetrates, sensitive strain gauges transmit electronic measurements of resistance to penetration of the cone tip and friction sleeve to an automatic data acquisition system. Measurements of the lateral drift of the cone are also obtained during the sounding via a built-in inclinometer. The test was recently standardized by the American Society of Testing and Materials (ASTM, D-3441 79). An alternate design which incorporates a piezoelement in the cone tip is often used for environmental studies. The piezoelement has the ability to measure the pore water pressures in the soil that are developed during penetration. Ground water sampling cones (Figure 2) are also capable of monitoring pore pressure and are discussed in greater detail below.

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Digital output of soil measurements are printed continuously during the sounding. All data are stored on a magnetic medium for future processing, and a graphical presentation of the data is immediately available for in-field stratigraphic correlation and evaluation. This feature allows testing to be concentrated in critical areas. Field plots consist of cone tip resistance, sleeve friction resistance, friction ratio, pore pressure, and differential pore pressure ratio. The interpretive data are compatible with most personal computer systems for further data reduction, including stratigraphic cross sections and contouring.

Ground water sampling cones are used to obtain selected samples of in situ gasses and liquids, retaining volatile components. Samples are encapsulated for easy and accurate lab analysis, minimizing external contamination.

The equipment is ideal for determination of the vertical and lateral extent of contamination. Tracer tests are often conducted where the system is used for the controlled injection of a tracer fluid. The spread of the fluid can then be observed by repeated sampling at various distances from the point of injection (Torstensson, 1984; Torstensson, et al., 1986). The major advantages of the electronic cone penetrometer over conventional sampling and testing are speed, continuous data measurements, economy, and reliability.

A typical field program consists of an initial site survey with the cone penetrometer, followed by a limited number of soil borings. One of the disadvantages of CPT equipment is the lack of soil samples for testing. Although near-surface samples are easily obtainable via a sampling adapter, its depth capability is limited. The cone penetrometer will, however, define the optimum depth and location for samples to be taken, thereby reducing the high cost normally associated with soil borings.

With the incorporation of the piezoelement into the system, the cone penetrometer has become an accepted, cost effective tool for environmental site assessments. Additional information on the use of piezocone data including discussions on corrections for pore pressure effects and normalization of data can be found in Robertson, et al., 1986.

Use of the Cone Penetrometer: Case History

A large truck mounted electronic cone penetrometer was used to collect data at a site in the southwestern United States. Based on limited data from a few monitoring wells at the site, an extensive survey of the subsurface was conducted using the CPT equipment. Data from the survey included detailed stratigraphy, soil types and properties, estimates of hydraulic parameters such as transmissivities and potentiometric surfaces, and the vertical and lateral extent of contamination. These data were then used to simulate contaminant infiltration and transport at the site, and to begin design of a remedial strategy for the aquifer. The objectives of the modeling effort were to simulate the extent of the contaminant plume, and to examine the effectiveness of various remedial schemes.

The CPT data showed the stratigraphy at the site to consist of an upper clay layer extending 30 feet (ft) below the ground surface. This clay was underlain by a sandy aquifer approximately 40 ft thick, which was in turn underlain by another clay layer of undetermined thickness.

Transport Concepts - Upper Zone

The upper clay at the site was relatively tight, with hydraulic conductivities averaging 10^{-6} centimeters per second (cm/sec), and ranging from

10^{-5} to 10^{-9} cm/sec. The rates of vertical migration were governed mainly by rainfall and infiltration processes within the unsaturated and saturated zones of the upper clay unit, and were computed analytically. The average water table elevation in the clay was approximately 5 ft msl, whereas the average elevation of the piezometric surface in the sand below was approximately 3 ft msl. Darcy's equation was used to calculate velocity and travel time of contaminants through the upper clay to the lower sand. The computations showed that for average hydraulic conductivities at the site, contaminants may require from 22 to 220 years to reach the sandy aquifer.

Once the contaminants in the clay travel to the base of the clay layer, they enter the sand, in which horizontal transport dominates.

Transport Concepts - Lower Zone

The sandy aquifer at the site comprised the lower zone for transport. The general direction of flow in this zone was horizontally to the west. Velocities in the sand, as indicated by observed perchlorethylene (PCE) values, appeared to be relatively low. Measured values indicated that the contaminants had migrated about 300 ft from the source area. In modeling this site, several transport mechanisms which may also affect the movement of the contaminants through the sands were not considered including adsorption, chemical reactions, and biodegradation. The exclusion of these mechanisms normally produces a conservative result.

Description of the USGS Ground Water Model

One of the most widely used two-dimensional ground water transport models is by Konikow and Bredehoeft (Konikow, 1978). The USGS method of characteristics (MOC) model simulates solute transport in flowing ground water and can be applied to a wide range of problem types involving steady-state or transient flow. The model computes concentration changes over a grid with time caused by advection and mixing (dispersion) from fluid sources. The model allows the solute to adsorb or degrade linearly, and assumes that the gradients of fluid density, viscosity, and temperature do not effect the velocity distribution. However, the aquifer may be heterogeneous and/or anisotropic with variable pump rates or head values.

The program uses an iterative alternating direction implicit (ADI) procedure to solve a finite-difference approximation to the ground water flow equation. After the head distribution is computed, the velocity of the ground water flow is computed for each node using an explicit finite-difference form of Darcy's equation. The model then uses a particle-tracking procedure to represent advective transport and a two-step explicit procedure to solve a finite-difference equation that describes the effects of hydrodynamic dispersion, fluid sources and sinks, and divergence of velocity.

Input parameters for the model include: transmissivity, porosity, storage coefficient, longitudinal and transverse dispersivity, grid system and overall geometry of boundary conditions, locations of sources and sinks, wells, boundary conditions, and initial conditions for heads and background concentrations.

The model output can include 2-D head distributions, the x and y velocity distributions, the drawdown depths, the concentration values at each grid location, and detailed breakthrough curves at selected observation wells. In order to analyze the model output, a graphical array package was used. This package, Biograph, is being developed at Rice University (Newell, 1988) as part of a Decision Support System for ground water modeling. It displays numerical data over the model grid as patterns varying in darkness: darker patterns represent higher values. The program also allows the user to graph values versus time (breakthrough curves), or over a cross section across the grid. Many of the figures in this paper are printed output from this package.

Initial Model Setup

A 19 by 25 grid of cells 50 ft on a side was set up and located in an east-west direction. The source area is located toward the eastern end of the grid. The overall length and width of the grid were 1250 ft and 950 ft, respectively, giving a simulation area of approximately 27.3 acres. The grid setup is shown in Figure 3.

The hydraulic conductivity used in the base run simulation was 0.0052 cm/sec, based on aquifer tests and CPT data at the site, and was assumed to be constant and isotropic throughout the aquifer. The longitudinal and transverse dispersivity values used in the base run were selected from the literature and set to 10 ft and 1 ft, respectively. An early investigation of the effects of variable thickness showed little effect, so a constant sand thickness of 40 ft was used. Finally, the background concentrations in the region were assumed to be negligible.

The source area was simulated in the model using injection wells in cells designated as source areas. The source cells used are shown in Figure 3. The leakage rate from the source into the aquifer was estimated using Darcy's law, and the extent of observed PCE. The final estimate was 0.0006 cubic feet per second (cfs), or 0.27 gallons per minute (GPM). The contaminant concentrations were calculated as a percentage of the source concentration, which was taken to be approximately 66,000 micrograms per liter (µg/l), based on observations in a monitoring well near the source and solubility data for the chemicals involved.

The hydraulic conditions in the aquifer were assumed to be at steady state in all of the simulations presented here. This assumption greatly reduces run times, and seldom produces any effect on model results. The validity of this approach was verified using the model in a hydraulically transient mode.

The period of time since the contaminants first reached the sand layer was difficult to determine. A simulation time of 5 years was chosen based on records of source activity, and on initial model results which indicated that approximately 5 years of contaminant movement were required to match observed data points.

Sensitivity Analysis

The model was run using the parameters described above to produce a base run to be used as a base line for comparison in the sensitivity analysis.

Three additional runs were made in order to investigate the sensitivity of the contaminant plume to changes in model parameters. The results of these runs are compared to the base run in Table 1. The table shows that the model is most sensitive to the source leakage rate, and shows little response to changes in other parameters.

Model Calibration

The goals of the hydraulic calibration effort were to simulate the general direction and velocity of the ground water in the area of interest. Water level contours, plume extent, and the geologic nature of the aquifer system were all used to develop a satisfactory "match" between reality and simulation.

The final calibration was achieved using constant head cells around the grid perimeter, and three additional cells representing local peaks and depressions

(Figure 3). The head values from the model output were entered into a contouring package, and the resulting contours were overlaid on the contour map created from observed head data. The final match presented a close correlation, as shown in Figure 4.

The observed data for PCE were chosen as the data to which the contaminant transport results of the model would be compared. This was only a preliminary calibration process, as normally at least 6 to 10 observed data points are required within the plume to calibrate a 2-dimensional model. Measurements from one monitoring well and two CPT points were used for comparison. Assuming a source concentration of 66,000 μg/l, the observed PCE concentrations as percentages of the source concentration in three model cells would be:

Cell	% of source concentration
7,9	0.333
10,13	0.355
8,13	0.0167

The results of the final model run are shown in Figure 5. The concentrations in the above three cells are 0.5%, 0.8%, and 0% of source concentration, respectively. The run shows good areal agreement, and is satisfactory based on the available data. The parameters used in this final run were:

Hydraulic Conductivity : 0.00052 cm/sec
Sand Thickness : 40 ft
Leakage rate : 0.0006 cfs
Time : 5 years
Longitudinal Dispersivity : 5 ft

In addition, the source area in the model was slightly reduced. The leakage of contaminants into cells (8,8) (9,8) and (9,10) was eliminated, effectively reducing the source area by 7500 square feet.

Remedial Design Criteria

Based on the CPT data collected at the site, several remedial techniques were found to be infeasible because of the depth of the contamination. These included a collector trench for contaminant removal, and slurry walls or sheet piling for plume containment. It was determined that the installation of a recovery well field was the only economically feasible option. A recovery field may include the installation of extraction and injection wells: extraction wells to reverse the gradient, and injection wells to increase the gradient and expedite the remediation time. The number of wells and the pumping rates required for a 5-year cleanup operation were investigated by numerical modeling.

Remedial Modeling - Basic Scenario

As an initial design of the extraction well field, three pumping wells were simulated approximately 75 ft down-gradient of the source area, spaced 150 ft apart. These locations in the model grid are shown in Figure 3. The wells were operated for 5 years. The results of operating these wells at various pumping rates are shown in Table 2. A longitudinal cross section of the plume through time for the run labeled "Low Rate 2" is shown in Figure 6. The table shows that the 3-well scheme is probably inadequate for a 5-year cleanup operation.

Additional Wells

Due to the lack of response from the 3-well system, four additional wells were placed in grid cells (8,9) (10,7) (12,5) and (11,8) and the pumping rate in each of the wells was increased to 3.5 GPM, which produced drawdowns of up to 20 ft. The source area was assumed to have been removed. After 5 years of pumping, the maximum concentration in the grid was reduced to 0.1%, and the plume area was less than 0.3 acres. A longitudinal cross section of the plume through time is shown in Figure 7. The plume after 5 years is shown in Figure 8.

Conclusions

After reviewing all available hydrogeology, CPT and monitoring well data for the site, it was possible to successfully model the migration of contaminants in the sand. Although the calibration of the model was based on limited data, the results of the remedial design effort are indicative of the scale of the remedial systems to be examined. In addition, the modeling effort at the site has exposed several areas where data were inadequate, and has shown which design options must be investigated further.

The availability of the CPT equipment has proven extremely useful in the investigation of this site, and can be used to collect the additional data required in order to complete the design of the remediation scheme. In order to fully utilize the power of the CPT method, communication must be increased between modeling and data collection stages. After the initial site survey, the investigation should iterate between modeling and data collection steps, with each step directing the efforts of the next. This combination of two powerful technologies can provide cost savings through increased productivity and efficiency, and is a concept which applies in all engineering disciplines.

Disclaimer

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Table 1. Sensitivity Analysis

Run Number	Parameter Changed (units) (base run value) (modified value)	Maximum Concentration (%)	Plume Area (Acres)
1	Hydraulic Conductivity (cm/sec)		
	0.0052	85	4.4
	0.00052	100	4.8
2	Source Leakage Rate (cfs)		
	0.0006	85	4.4
	0.0001	27	2.9
3	Longitudinal Dispersivity (ft)		
	10	85	4.4
	1	90	3.0

Table 2. 3-Well Remedial Scenario

Run Description	Source Removed	Pumping Rate (GPM)	Maximum Concentration (%)	Plume Area (Acres)
No Action 1	No	0	100	7.5
No Action 2	Yes	0	100	4.4
High Rate	No	4.5	76.4	3.2
Low Rate 1	No	1	99.8	4.6
Low Rate 2	Yes	1	89.4	4.3

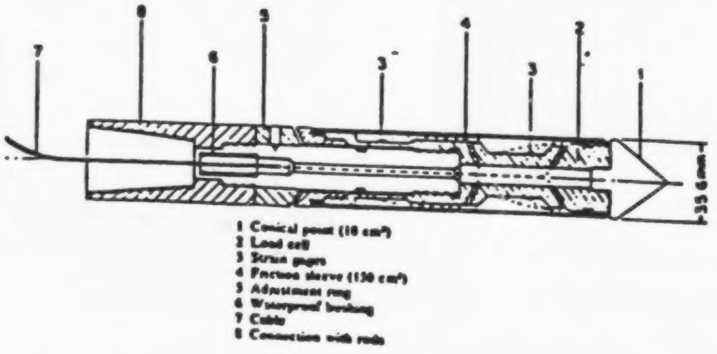

8
5
7
6
3
4
2
3
1
35.6 mm
1 Conical point (10 cm²)
2 Load cell
3 Strain gages
4 Friction sleeve (150 cm²)
5 Adjustment ring
6 Waterproof bushing
7 Cable
8 Connection with rods

Figure 1: Electric Friction Cone (after ASTM)

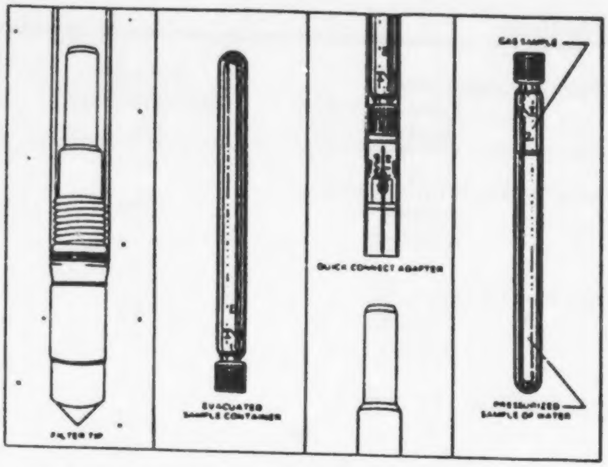
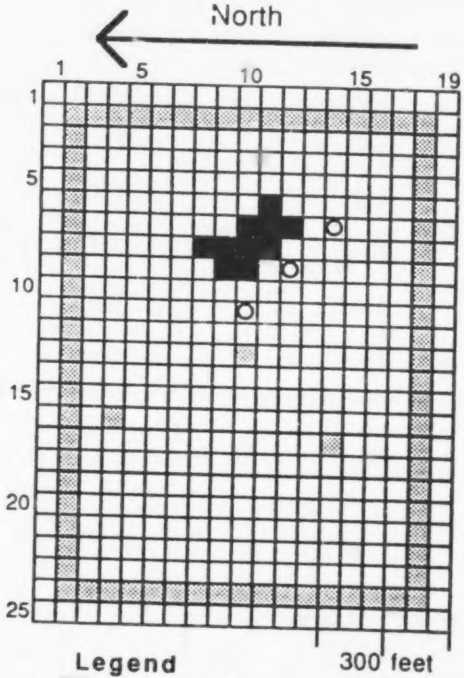

GAS SAMPLE
FILTER TIP
EVACUATED SAMPLE CONTAINER
QUICK CONNECT ADAPTER
PRESSURIZED SAMPLE OF WATER

Figure 2: Ground Water Sampling Probe
(courtesy of BAT Envitech)


North
1
5
10
15
19
1
5
10
15
20
25
300 feet

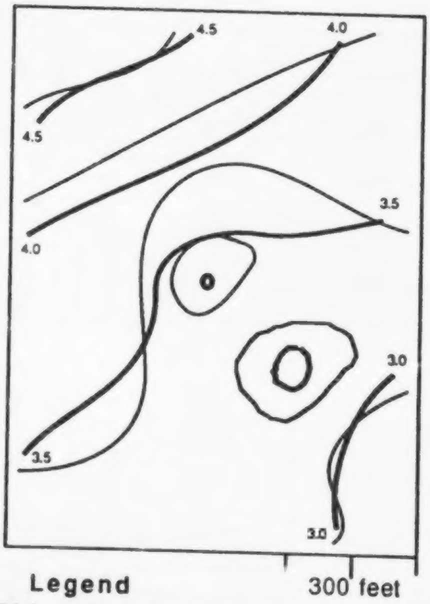
Legend

■ Source Cell

▨ Constant Head Cell

○ Pumping Well Location

Figure 3: Grid Setup


4.5
4.0
4.5
3.5
4.0
3.0
3.5
3.0
300 feet

Legend

Thick contours based on computed values

Thin contours based on observed values

Contour values in ft msl

Contour interval - 0.25 ft

Figure 4: Head Calibration

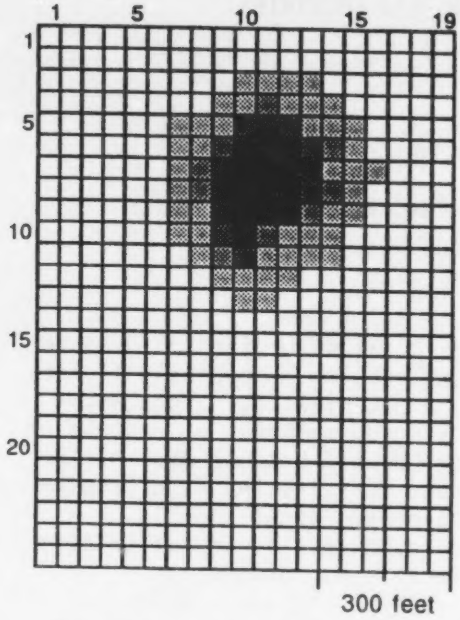


Figure 5: Calibrated Plume

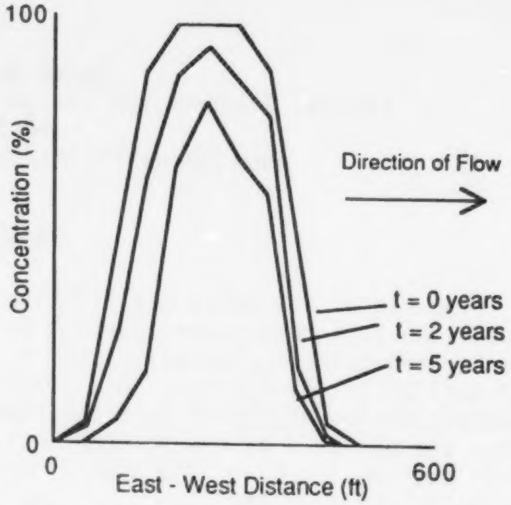


Figure 6: Cross Section through Plume - 3-Well Pumping Scenario (run description: Low Rate 2)

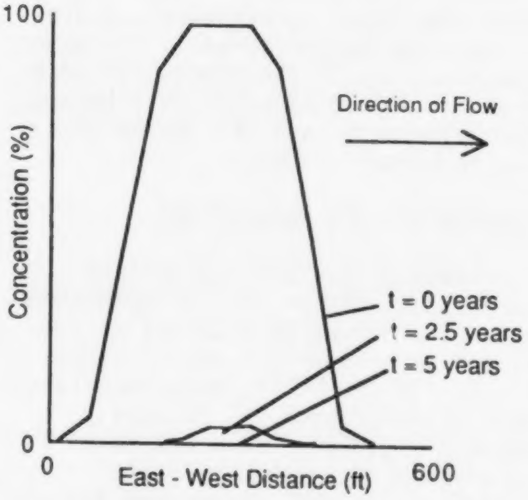


Figure 7: Cross Section through Plume - 7-Well Pumping Scenario

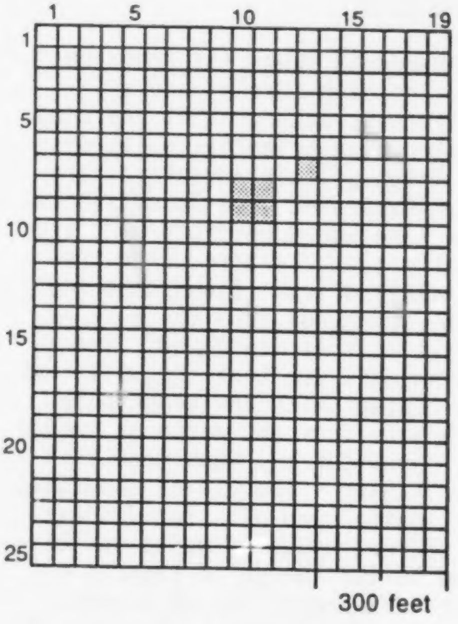


Figure 8: 7-Well Pumping Scenario - Plume after 5 Years

USE OF ABANDONED COAL/LIGNITE OPEN PITS FOR WASTE DISPOSAL IN SELECTED EUROPEAN COUNTRIES

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ABSTRACT

The use of abandoned coal/lignite pits as disposal sites for solid waste appears to be a reasonable approach to a difficult problem, especially if they are located close to the waste source. However, a potential for groundwater and soil pollution exists. This issue was discussed by a "Group of Experts on Opencast Mining of the UN Economic Commission for Europe" because most of the sites are operated by mining companies. This paper contains the major topics of discussion including the significance of the problem, legal aspects, characteristics of the open pits, waste intended for disposal, investigations required to obtain a disposal permit, disposal techniques, protection measures, monitoring environmental impacts, and research trends. A few countries are used as examples.

INTRODUCTION

Abandoned open pits from the extraction of minerals such as coal/lignite, sand/gravel, and clay, are attractive potential waste disposal sites. Their advantages are that an excavated area is available, no new land would be disturbed, and the waste can be placed below the original land level (landscape may even be improved), and the risk of fugitive dust is minimized. The disadvantages are that the waste may be in contact with the groundwater, or leachate from the waste may reach the groundwater and thus result in its pollution. The use of abandoned coal/lignite open pits for disposal of different types of waste was discussed in the "Group of Experts on Opencast Mining of the UN Economic Commission for Europe." The aim of the discussion was to compare legislation and regulations, current procedures, environmental impacts that have been found, protection measures in use, and future trends. The major contributions to the discussion were from the United Kingdom (UK), Poland, Czechoslovakia, and the German Democratic Republic (GDR).

LEGISLATION AND REGULATIONS

Both in Eastern and Western European countries, use of abandoned open pits for waste disposal is subjected to different laws and regulations. In the UK the most important one is the Disposal of Poisonous Waste Act (1972). This Act makes it an offense punishable by heavy penalties, to deposit on land any poisonous, noxious, or polluting substances which can give rise to an environmental hazard or cause danger to persons and animals. The Act gives responsibilities to waste manufacturers and disposal operators, especially regarding chemical composition of the disposal and its location as well. The other one is Control of Pollution Act (1974) which sets out arrangements for disposing of controlled waste, and duties of disposal authorities, and regulations under which the waste may be deposited. The subordinary to this Act, Regulations of 1976, detail the licensing of Waste Disposal (1976). According to this last one the disposing of waste, other than mining and quarry waste, require an application with listed waste volume, detail characteristics, type of containers, and their number, size and description. Moreover, the name of the person/employer who brought the waste to the disposal must be specified. The disposal of less hazardous waste such as colliery waste, fly ash, and domestic waste are the subject of the Town and Country Act (1971) and the Town and Country Planning Development Order (1979). According to the above provisions, permission for disposal is required, and mining authorities must consult with appropriate water authorities on all planning and applications. Finally in the UK, the Council of European Communities Directive for Groundwater Protection Against Pollution caused by Dangerous Substances (80/86) EC) has to be observed.

In Poland disposal into open pits is subjected to several laws such as: Environmental Protection Law (1980), Land Management Law (1985), Farmland and Forest Protection Law (1982), Water Law (1974) and finally the Mining Law (1978). Each of these laws is supplemented by many detailed regulations edited by the responsible ministries and local authorities. There are eight major steps in obtaining a permit.

1. A Feasibility Study that shall contain the characteristics of waste, characteristics of disposal site (geology, hydrogeology, surface water, geotechnics, dimensions, location, etc.), method of disposal, forecast of impact on the environment, protection measures, monitoring, and further research. This study is conducted by a consulting company.

2. An application of the waste disposing company to the Province Authorities for approval of a location. Ask whether a given waste can be stored in a given place, and what conditions must be met (the Feasibility Study must be enclosed).

3. The Application is reviewed by various departments of the province administration (Protection of Environment, Health, Regional Development. Transportation, Agriculture, etc.) and county/community administration. The Province and Local Councils (elected bodies) also review the application. The province authorities give their opinion on the site and list their requirements, and if necessary, they request further research or collection of information.

4. A General Technical Plan which discusses in more detail the subjects in the Feasibility Study, responds to the recommendations of the Province and Local Authorities, and presents results of any additional research that may have been performed.

5. Final application to the Province Authorities for the permit (the General Technical Plan is enclosed) is made.

6. The Authorities review the application using the procedure similar to the one given above (3.), and approve the Realization Plan with comments and recommendations.

7. Detail designs of the site are made, e.g., sealing, road construction, electrical power supply, and water management.

8. Disposal takes place with periodic inspection of the Province Authorities. They check to see that their recommendations and conditions are being met.

In the GDR Law, wastes are divided into three groups: toxic, polluting, and low or non-toxic ones. Only the third category is allowed to be disposed in open pits. This is regulated in general by the Environmental Policy Act, Water, Act, Matter Act, Mining Act, Toxicity Law, and in details by the Regulations. In the GDR, the laws require a study of waste reuse (recycling) prior to disposal application. The permission is always issued for a fixed period of time, fixed volume of wastes and disposal procedures.

In all the above countries permission is granted or confirmed by local authorities, and it includes the conditions, stipulations, and responsibilities of the company, even if there is more than one user of the site. In Eastern European countries laws and regulations are not as common as in Western Europe. In several European countries (Greece, Turkey, Yugoslavia, and others) there are no regulations.

Characteristics of the Open Pits used for Disposal

The open pits designated for waste disposal in Europe can be divided into two general groups. The first group are the open pits after bituminous coal extraction and will be represented here by examples in the UK.

Typical void dimensions and capacities for waste disposal are:

1. 400 x 400 m x 15 m (depth), 1,1 mill. m^3 capacity

2. 450 x 425 m x 56 m (depth), 3,0 mill. m^3 capacity

3. 1000 x 350 m x 80 m (depth), 15,0 mill. m^3 capacity.

The surrounding rocks are mostly shales, sandstones, and limestones. The second group are the open pits after lignite extraction, and here two types can be distinguished. The first ones are the final voids with an area of 50 - 800 hectares, depth 20 - 60 m and capacity up to 30 mill. m^3. The second ones are deep open pits which can have an area of 1000 hectares, depth 200 m and capacity up to 500 mill. m^3. The rocks surrounding lignite open pits consist mostly of sands and clays, both occurring in the slopes, and in the bottom of the void intended for waste disposal. Very often the aquifers are in potential contact with waste and are widespread and must be protected by law. Therefore, in all countries with environmental laws, obligatory waste disposal in these pits is restricted to the types of waste, as well as the disposal procedures and protection measures.

Characteristics of Waste Disposed in Open Pits

Due to the large size of abandoned open pits, reliable sealing would be very difficult and expensive; therefore the hazardous wastes of high toxicity are mostly banned from these sites. The most common use is the disposal of coal refuse (Poland, UK), fly ash from coal-fired power plants (most of the countries), domestic refuse (many countries), discards (Poland, UK, Czechoslovakia, construction/demolition materials (UK, Czechoslovakia), and wastes from briquetting factories (GDR).

Some examples of these wastes are presented below. The coal refuse has leachable TDS 500 mg/kg, Cl 50 mg/kg, SO_4 40 mg/kg, Phenols 0.06 mg/kg, CN 0.005 mg/kg, Zn 0.18 mg/kg, Cu 0.04 mg/kg, Pb 0.04 mg/kg, Mo 0.03 mg/kg, Cr 0.067 mg/kg, As 0.002 mg/kg, Sr 0.08 mg/kg, Hg 0.01 mg/kg, Cd 0.05 mg/kg.

The ash from the lignite-fired power plant contains leachable TDS up to 1000 mg/kg, and respectively Cl 100 mg/kg, SO_4 2000 mg/kg, Cu 0.75 mg/kg, Cr 0.93 mg/kg, Pb 0.8 mg/kg, Ni 1.0 mg/kg, Zn 5.2 mg/kg, Co 1.8 mg/kg, Cd 0.18 mg/kg, and Mo 0.75 mg/kg. These figures refer to the fresh ash. After disposal, the leachable heavy metals change from easily leachable oxides to less leachable carbonates. In some places where metallurgical discards are stored in open pits, high content of heavy metals, for example, Cr up to 10 mg/kg have been found. The domestic household wastes contain plastic, cans, paper, food, ash, etc., and may contain small amounts of hazardous waste disposed of with the household waste, for example; pesticides, solvents, and batteries. To conclude; in European countries the hazardous toxic wastes are not disposed of in the open pits. Only less toxic wastes are allowed; however large volumes of these wastes (up to a few million tons per year in one operation) can be very hazardous, even if toxicity per one ton of waste is relatively low.

Waste and Site Investigation

In all countries waste must be investigated prior to obtaining permission for its disposal. Results of the investigation have to be included in the application submitted by the company responsible for the disposal. In the waste investigation, special emphasis is put on their future reuse (GDR), to ascertain its risk of toxicity, and the categorization of substances containing harmful metalloids and metals that could have effect on groundwater (all countries). In Poland, for example, there are no precise regulations unequivocally defining the waste investigation techniques. The planning organization recommends an investigation in relation to the given site and disposal method. The investigation of precise chemical composition is not recommended, but investigation of waste leachability under the conditions within the disposal area are recommended. Tests under full saturation and/or only periodical leaching by rain water, are recommended. It is possible to obtain quick results from glass columns (diameter of 10 cm and 1 m long, and intensive leaching for 72 or 96 hours. More precise results can be obtained in a lysimeters study (e.g., lysimeters of a diameter of 1 m and 3 - 4 m high), which are leached in the natural rain conditions during the whole year. The chemical analysis of leachates shall cover all possible components that can be observed, including heavy metals and organic compounds. All possible toxic compounds are listed on the special official list. Basic site investigation is undertaken before open pit mining operations commence, to determine the hydrogeological conditions in the vicinity and they are usually continued during mining operations. During these operations other experiences also are gained, which can be used in the disposal site studies. Some additional site investigation is also done prior to disposal if the information from the mining period is not adequate. In Poland the following data are recommended for site evaluation.

1. Characteristics of aquifer having contact with waste disposal (thickness, areal extent, hydraulic conductivity, permeability and

specific yield).

2. Distribution of hydrodynamic heads,

3. Chemical composition of natural groundwater examined during the whole year prior to disposal (seasonal changes in the aquifers close to the surface are significant),

4. Lithology of aquifers in the aspect of absorption and ion exchange,

5. Detailed description of the open pit with respect to permeability of its bottom and slopes,

6. Identification of climatic conditions, especially water balance, and rain water infiltration rate.

7. Present and future use of groundwater in the disposal area.

All the above data regarding the waste and open pit characteristics must be included in the application for disposal permission. In GDR, a special official certificate is to be prepared for the locations.

Disposal Techniques

Deep mine colliery waste and discards are handled by train cars or trucks and spread with use of bulldozers. Ash from coal-fired power plants is handled as slurry by pipelines, as dry, by special tight train cars or trucks (then spread with water jet) and as semi-dry by belt conveyors (spread with spreaders). Domestic waste is contained in plastic bags (UK). Industrial waste, other than building rubble, that can cause pollution of groundwater is contained in sealed steel drums, sometimes pvc.

Dry wastes are always disposed of by "layer tipping." The thickness of layers doesn't exceed 1 m (UK) and about 5 - 10 m (Poland). Layers are compacted and sealed if necessary. In cases where spontaneous combustion is expected, the layers of waste are always sealed with clay. A very special technique of ash disposal in an active open pit has been applied in Poland. In the Belchatow mine-mouth operation, 38 million tons of lignite mined from one open pit is fired in the nearby power plant of 4320 MW capacity. About 4 million tons of fly ash containing leachable sulphates and heavy metals has to be disposed of within the internal dump of a still active open pit. The open pit is 200 m deep and both of its slopes and bottom are in 70 percent sand. The groundwater table is a widespread aquifer (both in overburden and under the mined lignite seam) and has been drawn down by 200 m for mining operations. It is kept below the pit bottom. Mine water is discharged, after treatment, to a protected river. After mining is completed, the groundwater will again saturate the overburden and ash disposal. Thus the aquifer must be protected forever. Sealing of such huge open pits (dumping of about 130 million m^3 of overburden plus 4 million tons of ash per year) is impossible. An extensive study of the problem showed that the waste should not be slurry-dumped due to the excess of polluted water, and its possible leaching to the aquifer; and not dry-ash dumped due to the dust that would be created. The solution was a mixing of ash with 30 percent water in special screw mixers. It provides the consistency of a wet non-dusting substance. During about 30 minutes of handling on belt conveyors, the consistency becomes that of a slightly cemented globule. Two thirds of the ash is mixed in the proportion of 1.5 with clayey (70 percent) overburden. When this overburden is disposed of on special selected benches of the internal dump (underlain mostly by clays) it forms an almost impermeable structure. This way groundwater is protected now and for the future.

Protection Measures

Sealing of open pits is a major groundwater protection measure. Two types of sealing are in use. The first one is to cover the bottom and slopes of the open pit with a clay blanket. In the UK the clay blanket is about 1 m thick to prevent both the ingress of groundwater and the aquifer pollution. On completion of waste disposal the surface is sealed with about 1 m of clay blanket that is covered with subsoil, topsoil, and revegetated. In the GDR the thickness of a clay blanket must be at least 2m and it must have permeability of $k = 10^{-8}$ m/sec. On the slopes it must be at least 1 m above the highest natural groundwater table. In Poland there are no regulations about the sealing layer thickness, but in the plan its efficiency must be proved by hydrogeological and geomechanical calculations. In one of the completed lignite open pits (40 m deep) the sandy bottom was sealed with 5 m of clay, but in this case clay was easily available from a nearby active open pit. The second type of sealing used in Poland is the vertical cutoff slurry wall constructed down to a continuous impermeable strata. The strata must be continuous, at least 2 m thick, and have a permeability of at least 10^{-7} m/sec. Its presence must be proven by site examination. The depth of slurry cutoff walls can be up to 25 m with a thickness of 0.5 - 1.0 m, and a required permeability of 10^{-8} m/sec. An example of this is a disposal site of waste from a coal desulphurization plant located in the vicinity of the aquifer used as a potable water supply for a large city. For neutralization of some kinds of wastes the injection of approved chemicals is in use. A successful case in the UK is the injection sealing of deep colliery waste that was polluting the surrounding water. The operation was run in two stages. To a depth of up to 7 meters a 2.1 lime/cement slurry was injected under pressure through boreholes drilled in 2 m pattern. Deeper portions, below 7 m were sealed by injection of pure lime milk in a dosage of 5 tons per hole. This procedure improved the quality of the discharge to acceptable limits. Surface water impounded within the waste disposal is always under control. In case of hydraulic disposals the polluted water is in a closed circuit. The excess of polluted surface water is pumped to surface lagoons and treated before discharge to natural streams. This water must meet the required standards in all countries. For example in the UK it is TDS below 75 mg/dm^3, zinc below 0.5 mg/dm^3, mineral, oils and hydrocarbons below 5 mg/dm^3 and pH between 6 and 9.

In all countries the surface of the filled abandoned open pit must be sealed and revegetated. In one country (GDR) the abandoned open pits cannot be used for waste disposal if they are closer than:

- 2000 m to facilities of public health and food production and,
- 1000 m to residential areas, recreation and sports facilities.

Beside the technical measures discussed above, in some countries, e.g., Poland, the company intending to dispose waste in an abandoned open pit must pay to the local community 10 USD/T for the waste of category I (the most hazardous) $2.5/T for the waste of category II, $0.50/T for the category III (fly ash) and $0.25 USD/T for the category IV (coal refuse).

Monitoring

Monitoring of groundwater, surface water and sometimes air is required by law. It is effected mostly by the waste disposal operator under the supervision of state or local environmental authorities.

Groundwater is monitored in piezometric tubes. For sealed disposal sites in Poland the monitoring wells are located around the disposal:

- 20 m up gradient of the disposal site
- 30 m from the disposal site in an intermediate zone
- 50 m from the disposal down gradient.

In the case of unsealed disposals which can produce some groundwater pollution, the monitoring wells are recommended to be situated downstream 1 - 4 radial lines:

1 st well	50 - 100 m from the edge
2nd well	100 - 300 m from the edge
3rd well	400 - 700 m from the edge
4th well	800 - 1500 m from the edge

Sampling is recommended once per month to once per three months. The same frequency of monitoring is recommended for surface water outflows.

Air and plants are monitored, but there are no detailed regulations. Requirements of local authorities determine the type and frequency of monitoring.

Environmental Impacts

1. Air Pollution

It has been found that air is polluted at a distance of up to 500 m from disposal sites. The permitted standards for dust fall (250T/km^2/year) and admissible concentration of suspended dust in air (instantaneous value 0.5 mg/m^3 and 0.022 mg/m^3 - average during the entire year) have been exceeded at that distance.

2. Groundwater Pollution

Groundwater pollution around a coal waste disposal site located in an abandoned open pit is given in the table below:

Designation	Unit	Average concentration prior to disposal	Average concentration after disposal	Maximum concentration after disposal
pH		6.66	6.25	6.88
Conductivity	us/cm^2	247.1	460.72	801.0
TDS	mg/dm^3	169.2	329.13	550.07
Cl	"	15.08	40.84	72.73
SO_4	"	54.1	117.98	209.89
Na	"	7.84	33.50	81.99
K	"	2.77	5.51	11.31
Ca	"	16.26	34.11	53.60
Mg	"	4.95	10.23	17.39
Mn	"	0.24	0.266	0.79
Fe total	"	4.60	3.7433	8.75
NNH_4	"	0.43	1.22	2.47
PO_4	"	0.014	0.0244	0.053
CN	"	0.0049	0.0059	0.0172
Phenols	"	0.0034	0.0036	0.0066
Al	"	0.16	0.181	0.444
Zn	"	0.360	0.1672	0.497
Cu	"	0.023	0.0102	0.0313
Pk	"	0.0165	0.246	0.047
Cr	"	0.0064	0.0056	0.075
As	"	0.0168	0.0274	0.057
Sr	"	0.130	0.1472	0.216
Mg	"	0.630	0.6294	1.300
Cd	"	0.0024	0.0037	0.0058
Mo	"	0.0148	0.0083	0.024
B	"	0.032	0.0685	0.095

3. Surface Water Pollution

Surface water pollution is illustrated by the examples given below of leachates from a coal waste disposal:

	Disposal No. 1 mg/dm^3	Disposal No. 2 mg/dm^3
Effluent at the slope foot		
TDS	26999	25238
Cl	15200	12125
SO_4	1277	99
Ca	534	820
Mg	380	500

Surface water flow		
TDS	5100	2756
Cl	520	1046
SO_4	900	670
Ca	120	no data
Mg	220	no data

5. Soils and Plants Contamination

So far, soil and plants contamination by disposal of wastes in open pits below the terrain surface has not been investigated enough to draw any reasonable conclusions. The observations, analyses, and measurements carried out far above terrain surface show contamination of soil and plants. It is a different quantitative phenomenon and conclusions resulting from it cannot be applied to waste disposal below the surface (in open pit).

All of the above figures and facts show that even non-hazardous waste (in US categorization) can be harmful to the environment, especially when disposed of in large volumes, and in open pits where the contact with groundwater is easy. They prove also that abandoned open pits must be sealed before disposal of waste if contact of waste with groundwater and surface water is possible, and groundwater quality is under protection.

Research Needs

Research should be focused on:

- increase of reuse of mining and metallurgical waste to diminish their volume and make them less hazardous to the environment,
- different leaching procedures for more accurate evaluation of waste toxicity,
- improvement of open pits exploration,
- chemical treatment of waste (for example, by injection) for neutralization and reduction of permeability,
- and sealing efficiency.

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DESICCATION AND PERMEABILITY OF SOIL BENTONITE MATERIALS

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ABSTRACT

A series of experiments were conducted to study the effect of drying on the backfill materials constituted from bentonite and other soil components. To simulate the field conditions, one half of a specimen was subject to cycles of drying and wetting while the other half was kept dry. Solutions of aniline, phenol and hydrochloric acid were used as the liquids. Material containing 10 percent bentonite showed the most cracking. The largest cracks were formed with phenol and the smallest with water. Hydrochloric acid showed no cracks. The cracks were smaller when the soil mixture consisted of 5 percent bentonite, 10 percent kaolinite, and 85 percent sand. The cracks were further reduced in size and density when the proportion of kaolinite was increased to 20 percent.

All the cracks essentially closed when the specimen was subjected to permeability tests. Permeability tests on the cracked specimens did show some what higher values for the hydraulic conductivity. The permeability ratio of cracked to uncracked specimens ranged from about 2 to 25.

INTRODUCTION

Seepage has been successfully controlled in many field problems by providing a soil-bentonite backfill in slurry walls. Such walls are effective in controlling seepage at uncontaminated sites. A typical backfill mix consists of sodium bentonite, clay, and coarse grained materials. The mix is designed to achieve a permeability of 10^{-7} cm/sec or less. In recent years slurry walls are being extensively used for containment of waste sites. A literature survey shows that the effect of desiccation on the integrity of slurry walls still remains untouched. During its service life, the portion of a slurry wall below the lowest ground water level remains in a saturated state while the portion above undergoes drying and wetting cycles as a result of ground water fluctuation and precipitation. The degree to which the change in permeability in a particular zone occurs may be affected by the number of drying and wetting cycles, amount of precipitation, and volume of leachate generated.

PURPOSE

The purpose of this research was to conduct a series of experiments to study the effect of drying on the backfill materials constituted from bentonite and other soil components. The study was also to provide information on the size and distribution of drying cracks as affected by water and various organic and inorganic chemicals

APPROACH

Test specimens were prepared by one dimensional consolidation to a maximum pressure of 50 kPa (kilo Pascal). The consolidated specimens were 70 mm in diameter and 30 to 40 mm in height. For each soil mix three specimens were prepared for testing with each of the chemicals. One of the samples was maintained in a saturated state (S1) and subjected to permeability tests. The second specimen was allowed to dry in air and afterward placed in an oven at 40°C for 48 hours (S2). The third sample was subjected to wet and dry cycles (S3). After the desiccation studies these specimens were used for permeability tests (1).

Desiccation Study

The proportion of various soil-bentonite mixes are shown in Table 1. The chemicals and their concentrations are shown in Table 2.

Table 1. Design Mix.

Symbol	Bentonite (%)	Kaolinite (%)	Sand (%)
M11	10		90
M5	5	10	85
M6	5	20	75

Table 2. Chemicals

Symbol	Liquid	Concentration ppm or N
L2	Aniline	10000
L5	Phenol	10000
L9	HCl	1.0

Bentonite was thoroughly mixed with the given liquid to form a slurry and was allowed to activate for 24 hours. After that the slurry was mixed with other soil components and poured into a cylindrical plastic mould. Each end of the specimen was covered with a filter paper and a porous stone before consolidation.

Tests on dried backfill materials (2) showed that they had lower permeability than the nondried specimens. Since uniform drying does not represent field conditions, the method of drying was modified. The plastic mould for the desiccation tests consisted of two longitudinal halves held together by clamps. After completion of the consolidation the specimen along with its mold was laid on its side. The upper half of the mould was removed and the sample was allowed to dry out either in air at room temperature or in an oven at 40° C. At the end of the drying period liquid was added to the tray so that half the sample was submerged. The two ends of the specimen were kept covered with semicircular filter papers and porous stones to prevent any possible sloughing. The time for completion of one dry and one wet cycle ranged from 5 to 8 days or more in case of air drying. The wet and dry cycles were repeated as desired.

The sample subjected to this form of drying was considered to represent field conditions for a slurry wall. Finally the second half of the cylinder was also removed and the sample was mounted in a triaxial cell for the permeability measurements using the flow pump method.

Permeability Measurements

The permeability measuring equipment consisted of a stainless steel flexible wall permeability cell and air pressure system. Pore pressure parameter B= 0.95 was used for saturation. Permeability was determined using a constant rate of flow (3).

PROBLEMS ENCOUNTERED

In some instances the soil adhered to the consolidation mold. The adhesion was overcome by smearing the mold with silicon grease. Because of the low governing back pressure for the flow pump, both vacuum and back pressure were utilized for sample saturation. Considerable volume of flow was required to realize saturation.

RESULTS

Fig. 1 shows the state of the specimen from mix M11 containing 10 percent sodium bentonite and 90 percent sand after the third drying cycle with water. The first drying cycle showed only hairline cracks. After the second cycle the cracks were more clearly noticeable. But after the third cycle the cracks had become fairly wide. The largest crack developed horizontally along the wet-dry interface. Most of smaller cracks intersected the larger crack. During the wetting cycles the cracks appeared to close. But they opened up with greater intensity during the drying cycle.

Tests with phenol showed minor cracks at dry-wet interface with the very first dry cycle (Fig. 2). Cracks in the horizontal direction became more extensive at the end of the second dry cycle. As shown in Fig. 3 the cracks are also visible along the side of the sample indicating that they extended from one face to the other. As indicated in Fig. 4 with aniline the cracks were smaller even after the third cycle. No cracks were found with hydrochloric acid, only the color of the sample had changed.

There was only negligible cracking for mix M5 with water though some sloughing was observed in the zone which was subjected to frequent wetting. Only the sloughing appeared to increase with the number of cycles. As indicated in Fig. 5 phenol produced cracks. They were visible on both faces of the specimen. However, the cracks shown in the Fig. 5 are for the fifth cycle. When compared with Fig. 2 which shows cracks for only the second cycle, these cracks are much smaller. Fig. 6 hows the effect of aniline during the fifth cycle. The cracks are thin, horizontal and at the dry-wet interface. The lower section which underwent wetting and drying shows some cracks too. The cracks are still smaller as compared with mix M11 which had undergone only three dry-wet cycles . The difference in the cracking behavior may be attributed to the total percentages and the types of clays present in the two mixes. M11 contained 10 percent bentonite while M6 had 5 percent bentonite and 10 percent kaolinite. The reaction with hydrochloric acid was similar to that with M11.

There was not much difference in response of M6 which contained 25 percent clay as compared with M5.

In most of the cases the location and the pattern of the cracks were typical. Deep and wide cracks were observed at the wet-dry interface. The size, number, and the density of the cracks increased with increasing number of cycles. The organic chemicals showed larger cracks than water. Most of the time the cracks appeared to close upon wetting, but they became more severe as the wetting was followed by drying. No cracks could be detected with hydrochloric acid.

PERMEABILITY TESTS

The results of permeability tests are shown in Table 3.

Table 3. Results of Permeability Tests.

No.	k,cm/s	state	permeant
M11S1L1	3×10^{-9}	wet	water
M11S2L1	6×10^{-10}	dry	water
M11S3L1	6×10^{-9}	cyc	water
M11S1L2	2×10^{-9}	wet	aniline
M11S3L2	5×10^{-8}	cyc	aniline
M6S1L1	1.5×10^{-9}	wet	water
M6S2L1	1.6×10^{-9}	dry	water
M6S3L1	1.7×10^{-9}	cyc	water

For comparison purposes, the permeability of the soil samples were measured in wet, dry, and cycled state for some of the samples. For M11 the lowest permeability was for the specimen which was dried uniformly. Since drying reduces the void ratio and the subsequent swelling during saturation does not restore the original volume of the specimen, this should be expected. When the permeability of the specimen which was subjected to dry-wet cycles is compared with uniformly dried specimen it is one order of magnitude larger. Compared with the wet specimen the permeability of the cycled specimen is only twice as large. Considering the large and continuous cracks exhibited in Fig. 1 and Fig. 2, the increase in permeability appears inconsistent. A photograph of the same specimen (Fig. 1) after the permeability test is shown in Fig. 7. Note that none of the cracks that were visible in Fig. 1 are discernible. The combination of swelling during saturation and the confining pressure resulted in nearly complete healing of the specimen. Had the cracks been completely closed the coefficient of permeability would be of the same order of magnitude as the dry specimen.

With aniline the cycled specimen shows a greater increase in permeability over the wet specimen (25 times larger) when compared with water (2 times larger).

There was little difference in the permeability for M6 with water regardless of the state of the test specimen. Recall that the cracks with water were only marginal for this soil mix. No data is available on mix M6 with chemicals.

CONCLUSIONS

Based on the work done, the following conclusions may be drawn

1. For bentonite-sand mix the major cracks developed at the dry-wet interface. With the increasing number of cycles the density and the size of the cracks increased. During wetting cycles they appear to close.
2. The organic chemicals showed much larger cracks than water. Among the organics phenol displayed larger cracks than aniline.
3. The increased percentage of clay helped in reduction of the crack formation.
4. The permeability of the cycled samples was generally higher than the wet samples. The difference was more for the organics than for water.
5. The swelling of the cycled specimens during saturation combined with cell confining pressure resulted in closing of most of the cracks.

Disclaimer

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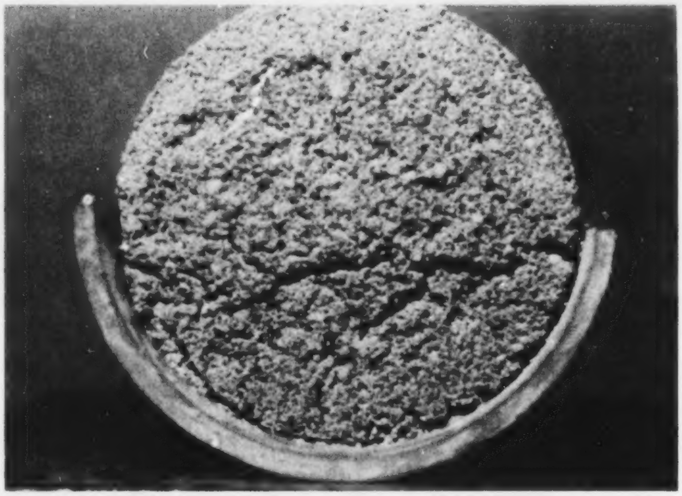

Figure 1. M11-S3-L1
after 3 dry-wet
cycles with water

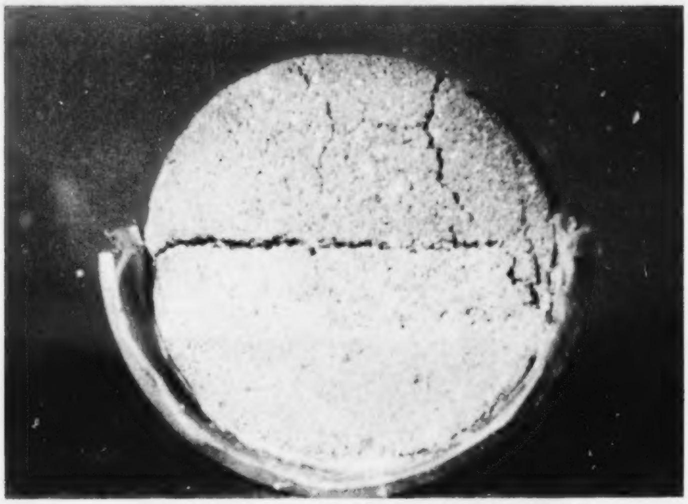

Figure 2. M11-S3-L5
after 3 dry-wet
cycles with phenol

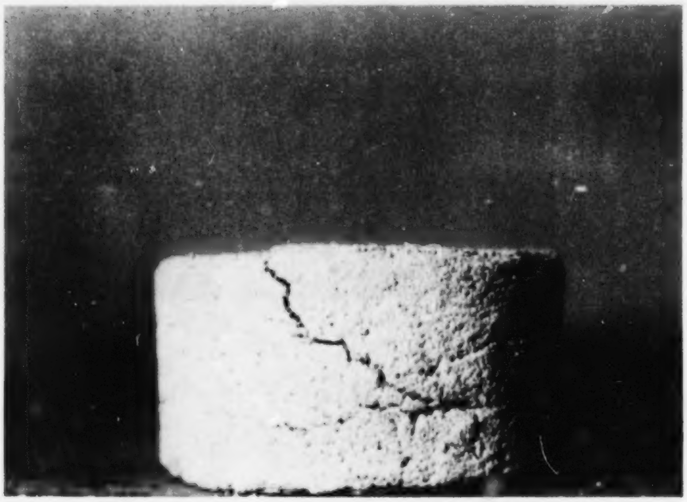

Figure 3. Side view
of M11-S3-L5

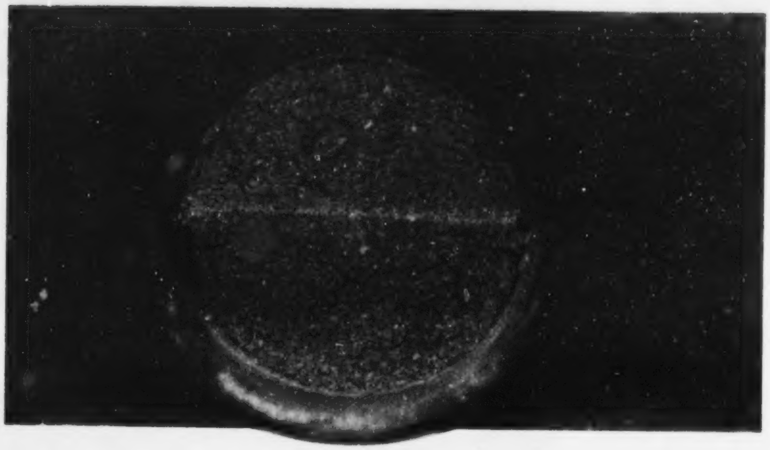

Figure 4. M11-S3-L2 after 3 dry-wet cycles with aniline

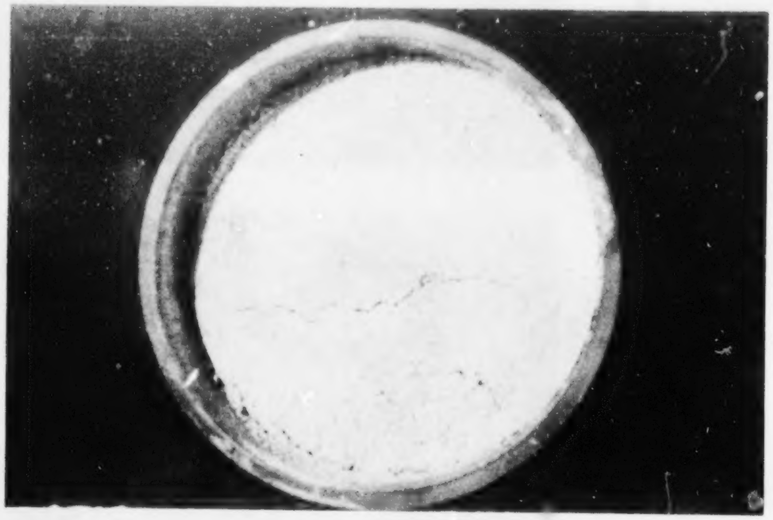

Figure 5. M5-S3-L5 after 5 dry-wet cycles with phenol

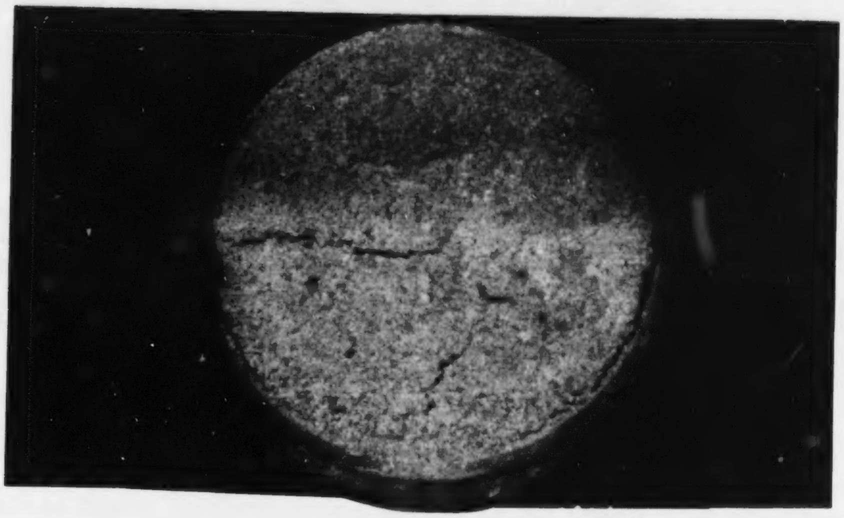

Figure 6. M5-S3-L5 after 5 dry-wet cycles with aniline

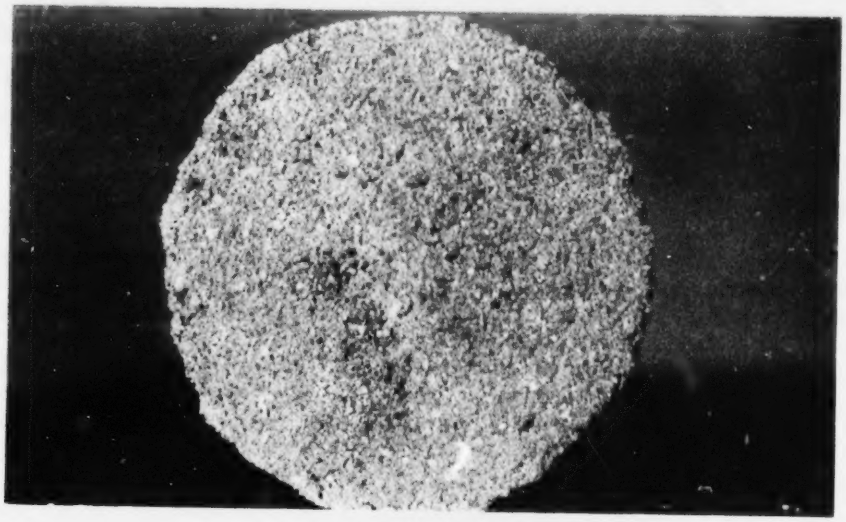

Figure 7. M11-S3-L1 after permeability test.

DESIGN OF CLAY LINERS TO MINIMIZE SHRINKAGE CRACKING

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ABSTRACT

Clay liners have been used to store hazardous liquid wastes or as back-up to plastic liners. The design of the clay liner mix is normally based on achieving a sufficiently low coefficient of permeability. This has been sometimes approached by mixing native soils with bentonite. Although the bentonite addition does reduce the permeability of the mix it also causes an increase of the shrinkage potential of the liner mix. This study has been focussed on the feasibility of reducing the shrinkage potential of the liner mix, while maintaining a sufficiently small permeability coefficient. The variables considered are the clay mineral used in the mix and the addition of coarse aggregate to form a stiff framework of grains that would resist the volume change imposed on the liner. The study also addressed the selection of the best gradation of coarse aggregate that would minimize the shrinkage potential.

For these purposes, specimens prepared by mixing bentonite or kaolinite with three alternative gradations of coarse aggregate were compacted under optimum conditions. The shrinkage strains experienced upon air drying of the specimens were measured, duplicates of these specimens were subject to permeability tests, and to a cycle of consecutive swell and shrink. The formation of cracks in the specimen subjected to the swell/shrink cycle was investigated by visual observation of the split specimens after staining the crack walls with methylene blue.

The results of this study indicate that the addition of inert clays or coarse aggregate to a liner mix are feasible means to reduce the shrinkage potential of the mix while maintaining a reasonably low permeability. The best gradation of coarse aggregate was found to be the gradation of the theoretical Fuller's curve for the maximum size of aggregate being used.

INTRODUCTION

The containment of hazardous liquid wastes is one of the most troublesome and certainly most urgent problems facing the industrial community. Existing regulations prohibit the disposal of free liquids unless the landfill has an adequate liner. The availability of suitable clayey soils in many regions of the United States makes the use of clay liners an economically attractive solution. Furthermore, clay liners have and can always be used as back-up for synthetic liners.

Clay liners have been normally built using native soils mixed with bentonite and compacted to form the liner. The bentonite is used to reduce the permeability of the liner mix to some small value. At present, the design of the liner mix is based on achieving a material with the desired permeability coefficient. However, the clay particles of bentonite are highly susceptible to changes in moisture content, to capillary forces, and to physico-chemical interactions with the liquid waste. Due to these effects, the properties and the structure of a compacted liner can change with time, resulting in a reduction of the effectiveness of the liner as a barrier to contain waste.

The deterioration of the liner can be the result of volumetric changes imposed by climatic wet-dry, or freeze-thaw cycles (1), or volumetric changes associated with the interaction of clay particles with the liquid waste (2).

The designer has practically no control over the magnitude of the changes that will be imposed on the liner; that is, the degree of desiccation the liner will undergo, or the concentration of the stored liquid waste. However, the designer can influence the formation and the extent of shrinkage cracks by manipulating the composition of the liner mix, in order to reduce the shrinkage potential of the compacted liner to a minimum.

PURPOSE

The primary goal of this study was to evaluate the feasibility of choosing liner mixes that minimize the shrinkage potential of the liner while the permeability is kept at some reasonably small value, such as 1×10^{-7} cm/sec (3).

The most obvious variable available to reduce shrinkage of the liner mix is the type of clay mineral used to mix with the soil. The shrink/swell behavior of compacted clayey soils has been related to the predominant clay mineral (4). The study has focussed on comparing the permeability and shrinkage behavior of liner mixes prepared with commercially available bentonite and kaolinite.

The inclusion of large sizes of inert ballast has been shown (5) to decrease the shrinkage potential of the soil mix. At the same time, the inclusion of large grain sizes is known to decrease the permeability of the mix (6), provided that the large size particles do not dictate an increase in the pore volume of the soil mix. The second goal of this study has been to evaluate the effect of large particle aggregates on the permeability and shrinkage potential of the soil mix and the selection of a best gradation that would maximize the improvement of both properties.

APPROACH

Materials

The specimens tested were prepared by mixing clay with coarse aggregate. The coarse aggregate was obtained by sieving crushed gravel and sand into five size intervals. The effect of the gradation of the coarse aggregate was evaluated by preparing and testing triplicate specimens with three different gradations. The specimens of Batch 1 were prepared with the gradation of Fuller's curve for the maximum size aggregate of 3/4 in. The specimens of Batch 2 and Batch 3 were prepared with gradations on either side of Fuller's curve. The coarse aggregate compositions of the three batches are presented in Table 1.

Table 1. Coarse Aggregate Percentile Composition of the Three Batches

Particle Size Fraction	Batch 1	Batch 2	Batch 3
3/4"-3/8"	31.37	46.94	22.99
3/8"-No.4	21.17	18.37	17.24
No.4-No.10	18.62	14.29	20.69
No.10-No. 40	18.79	13.27	22.99
No. 40-No.200	10.05	7.14	16.09

One set of batches was prepared by mixing the coarse aggregate with pure sodium-base Wyoming bentonite. A second set of batches was prepared with a local low shrinkage clay "kaolinite" that exhibits a liquid limit of 35.5 and a plastic limit of 20.1. Hydrometer analyses indicated that the kaolinite contained 30% of clay-size particles, 55% of silt-size particles, and 15% of fine sand. Although no mineralogical identification was attempted, the Skempton's activity coefficient of 0.5 is typical of a kaolinite (7).

Compaction Tests

For each trial mix, a compaction test was performed to determine the maximum dry unit weight and the optimum moisture content. All specimens for subsequent testing were prepared by compacting the mix at these optimum conditions.

A standard Proctor compaction test in a six-inch mold was performed for each trial mix. The mold was filled in three lifts, and the amounts of coarse aggregate and clay for each lift were weighed, mixed, and wetted separately to reduce the risk of segregation.

Shrinkage Measurements

Specimens of each trial mix were compacted, extruded from the mold, and left to air dry in a 30% relative humidity controlled room. The shrinkage of the specimen was monitored with a dial gage measuring the axial deformation, and a caliper was used to measure the changes in diameter. The drying process was prolonged until the dial gage measurements indicated that the volume changes had stopped.

Permeability Tests

The permeability of the trial mixes was determined on specimens compacted inside a section of a six inch PVC pipe. The specimen was then allowed to saturate by ponding permeating fluid in the pipe for about a month. Then the pipe was capped and connected to a standing burette to perform a series of falling head tests. The permeating fluid used was a 0.01 N calcium chloride solution. The hydraulic gradients during the tests ranged from 6 to 8. The tests were prolonged until a nearly constant coefficient of permeability was obtained in consecutive measurements. This period of time ranged from 3 to 4 weeks.

Consecutive Swell/Shrink Behavior

Specimens of the trial mixes were subjected first to swelling and then to a shrinking cycle. The swelling and shrinkage strains were monitored and the cycles were prolonged until the deformations had stopped. The comparison of the swelling and shrinkage strains allowed an indication of whether the swelling process imposed permanent changes on the compacted specimen.

After the shrinkage cycle, the specimens were stained with a solution of methylene blue deposited inside the shrinkage cracks with a burette. After staining and air drying, the specimen was split and the length of penetration of the stains through the specimen or the contact specimen-mold was recorded.

PROBLEMS ENCOUNTERED

One problem encountered in the measurement of shrinkage strains upon air drying the specimens was the axial deformation of the specimen due to its own weight. To assess the importance of this effect, concurrent measurements of the diametral deformation of the specimen were recorded. The deformations due to its own weight were very important in the specimens subject to swelling. This imposed the need to perform the swelling phase on specimens inside molds.

RESULTS

Specimens of each batch were prepared by mixing the fixed coarse aggregate gradations with increasing percentages of clay. A total of 20 trial mixes with bentonite and 28 with kaolinite were tested. However, some of the trial mixes did reach the desired coefficient of permeability, and further testing of the trial mix was cancelled. Due to space constraints, the results presented in this paper include only the trial mixes that were subject to all the tests described. The complete set of all the tests performed have been presented elsewhere (8). A summary of the tests results on bentonite trial mixes is presented in Table 2. Table 3 summarizes the test results on kaolinite trial mixes.

The maximum dry unit weights, obtained in the compaction tests, decreased for increasing clay content. This trend was very apparent in the bentonite trial mixes, but was less apparent for the kaolinite trial mixes shown in Table 3. However, the whole set of compaction test results on kaolinite mixes showed a slight increase of the maximum dry unit weight at low clay contents and, then, a general decrease towards larger clay contents.

The maximum dry unit weights obtained on Batch 1 specimens with bentonite were clearly larger than for the other batches. This indicated that Fuller's curve provides the more compact specimens; that is, it allows packing the maximum amount of clay and aggregate into the mix. The dry unit weights of kaolinite mixes were consistently larger than for bentonite mixes. This effect is related to the lower affinity for water of the kaolinite particles, thus, allowing a more compact specimen.

The permeability of bentonite specimens with small clay contents was very large. To reach an acceptable permeability coefficient, it was necessary to mix in about 6% clay for the gradation of Batches 1 and 2, and about 8% for the gradation of Batch 3. The addition of more clay did not reduce significantly the permeability of the mix. The differences in permeability shown in Table 2 are not significant and are within the accuracy of the determination.

The permeability of kaolinite specimens was larger than for the bentonite specimens. However, all batches showed a clear pattern of decreasing permeability with clay content, and with sufficiently large clay contents, they reached comparable permeabilities to the bentonite specimens. The change from high permeabilities to acceptable permeabilities for a liner was more gradual for the kaolinite specimens than for the bentonite specimens. This suggests that defects of mixing of the soils in the field could have a much less drastic effect when kaolinites are used instead of bentonites. The permeability tests on kaolinite specimens of Batch 1 achieved an acceptable (3) permeability with smaller clay percentages than Batches 2 and 3. This indicated that the gradation of Fuller's curve provided the best liner mix. The permeabilities of the specimens of Batch 3, corresponding to the more sandy gradation, were the largest and never reached an acceptable permeability even for the largest clay contents used.

The specimens left to air dry in a controlled environment experienced axial strains consistently larger than the transversal strains. This is believed to be the result of axial deformations of the specimen due to its own weight. Both sets of measurements indicated that the specimens decreased in length and in diameter during the drying process. For all batches and clay types,

Table 2. Summary of Test Results on Bentonite Trial Mixes

Batch No.	Percent Clay (%)	Maximum Dry Unit Weight (pcf)	Stable Permeability (cm/min.)	Strains Upon Air Drying		Strains in Swell/Shrink		Crack Continuity
				Axial (%)	Trans. (%)	Swell (%)	Shrink (%)	(%)[a]
1	6.05	128.0	5.25×10^{-7}	0.48	0.20	6.99	4.30	35.0
1	7.92	126.7	4.75×10^{-7}	0.90	0.37	11.05	5.99	100
1	9.79	126.2	5.25×10^{-7}	0.81	0.32	12.57	6.27	100
1	11.4	126.1	1.10×10^{-6}	1.12	0.37	11.81	7.75	100
1	13.1	126.2	7.90×10^{-7}	2.22	0.50	13.91	11.61	100
2	5.77	124.4	8.05×10^{-7}	0.50	0.18	5.90	2.47	100
2	7.96	123.0	4.05×10^{-7}	0.20	0.18	14.63	6.52	100
2	9.93	121.0	3.90×10^{-7}	0.74	0.32	13.52	5.17	100
2	10.9	119.1	2.45×10^{-7}	0.30	0.33	14.69	8.50	100
2	12.5	118.8	7.20×10^{-7}	0.65	0.27	17.53	10.03	100
2	14.0	118.3	5.80×10^{-7}	0.13	0.47	18.04	10.00	100
2	15.5	116.0	4.90×10^{-7}	0.74	0.20	17.08	11.86	100
2	16.9	116.3	4.70×10^{-7}	2.75	0.45	16.12	6.62	100
3	8.0	123.1	6.25×10^{-7}	1.29	0.40	9.00	6.02	100
3	10.0	121.2	6.50×10^{-7}	1.59	0.72	10.16	5.96	100
3	12.0	120.9	1.05×10^{-6}	0.73	0.43	13.37	7.57	100
3	14.0	117.5	9.45×10^{-7}	1.15	0.62	17.41	8.73	100
3	16.0	116.2	5.80×10^{-7}	1.10	0.77	17.99	9.39	100

[a] Indicates the length of the specimen stained with methylene blue as a percentage of the total length of the specimen.

these measurements indicated that the shrinkage potential of the mix increases with increasing clay contents. These results illustrate that the skeleton of aggregate was not able to completely prevent the shrinkage of the specimens. In order to achieve this goal, these results suggest that higher compactive efforts than the standard Proctor might be necessary. For comparable clay contents, the kaolinite specimens experienced smaller strains than the bentonite specimens. Thus, the use of kaolinite can help to reduce the risk or the extent of cracking of a liner.

The swelling strains of all three batches of bentonite specimens increased with increasing clay content. By way of contrast, the swelling strains of kaolinite specimens did not exhibit this trend. The shrinkage strains experienced by the specimens after the swelling phase were consistently lower for both clays and for all the batches. This suggests that the swelling process caused some irreversible changes on the specimen, thus implying that successive cycles of wetting and drying of a liner can induce a progressive change of the compacted soil structure. Although, both clay types exhibited these structural changes, both the swelling and shrinking strains experienced by the kaolinite specimens were smaller than those experienced by the bentonite specimens. Therefore, a liner built with kaolinite would be less affected by successive wet/dry cycles. The swelling and shrinking

Table 3. Summary of Test Results on Kaolinite Trial Mixes

Batch No.	Fine Grained Fraction (%)	Maximum Dry Unit Weight (pcf)	Stable Permeability (cm/min.)	Strains Upon Air Drying		Strains in Swell/Shrink		Crack Continuity (%)[a]
				Axial (%)	Trans. (%)	Swell (%)	Shrink (%)	
1	15.30	133.5	9.50×10^{-6}	0.07	0.57	8.65	3.90	9.5
1	17.00	133.4	7.00×10^{-6}	1.08	0.72	7.59	3.58	100
1	18.70	133.4	3.50×10^{-6}	1.20	1.02	8.38	3.69	100
2	11.93	137.3	3.09×10^{-2}	0.53	0.28	7.76	4.21	21.0
2	13.20	137.3	1.13×10^{-3}	0.24	0.15	13.98	6.73	31.6
2	14.42	135.5	1.05×10^{-4}	0.58	0.52	5.95	2.35	26.3
2	16.15	139.5	1.50×10^{-6}	0.35	1.05	6.64	2.83	10.0
3	8.50	133.5	3.60×10^{-2}	0.31	0.33	2.57	1.02	19.0
3	10.20	133.5	1.29×10^{-2}	0.21	0.32	6.47	2.96	18.2
3	11.90	134.2	4.53×10^{-2}	0.26	0.33	5.16	2.53	100
3	13.60	134.2	3.48×10^{-3}	0.50	0.44	4.61	3.07	28.6
3	17.00	136.1	1.20×10^{-3}	0.76	1.00	7.91	3.11	47.6

[a] Indicates the length of methylene blue penetration at the mold-specimen contact as a percentage of the total length of the specimen.

strains experienced by the specimens of Batch 1 were smaller than those of Batches 2 and 3, thus indicating that the gradation affects the potential changes induced by wet/dry cycles, and that a liner with a gradation adjusted to Fuller's curve will be less prone to a progressive deterioration by successive wet/dry cycles.

After the swell/shrink cycle, the bentonite specimens exhibited very apparent cracks uniformly distributed through the exposed surface of the specimen. By way of contrast, the kaolinite specimens did not crack, with only three exceptions of specimens showing a small crack at the contact between the specimen and the mold. When the methylene blue solution was deposited in the cracks of (almost all) the bentonite specimens, it moved through the crack very fast and appeared at the bottom of the specimen, thus indicating that the shrinkage cracks extended through the length of the specimen. From the observation of the split specimens, it was determined that the methylene blue had moved through the soil mass in some specimens and in others, after moving through the soil mass a fraction of the length of the specimen, it had moved to the contact mold-soil. The methylene blue solution did not penetrate through the soil mass of the kaolinite specimens in any measurable amount; the only observed path of penetration was at the mold-soil contact. These observations on the cracks of the specimens after the swell/shrink cycle are another indication that a liner built with kaolinites would be much less susceptible to be damaged by wet/dry cycles.

The larger cracks developed through the bentonite specimens are attributed to the extrusion of the bentonite out of the pores of the aggregate during the swelling phase. It was observed that, during the swelling phase, a soft layer of clay particles with a consistency of a gel was forming on the top of the bentonite specimens. This layer was not observed in the kaolinite specimens.

In summary, the results of the compactions tests indicate that the use of kaolinite, and adjusting the gradation of the liner mix to Fuller's curve, can provide a more dense liner; the permeability tests results indicate that it is also possible to achieve acceptable permeabilities for the liner when using inactive clays such as kaolinites; the shrinkage strain measurements indicate that a liner built with kaolinites will experience smaller strains upon drying and thus, will be less likely of cracking; the strains recorded during the swell/shrink cycles indicate that a liner built with kaolinite will experience smaller progressive damage and this will be further reduced if the gradation of the mix is adjusted to Fuller's curve. These considerations indicate that adjusting the gradation of the liner mix to Fuller's curve and using inactive clays such as kaolinites are feasible means to reduce the risk of liner damage by shrinkage cracking, while still achieving acceptable permeability coefficients.

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FIELD STUDIES ON THE HYDROLOGICAL PERFORMANCE OF MULTILAYERED LANDFILL CAPS

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ABSTRACT

Along with the remedial action on the waste disposal site Georgswerder in Hamburg (FRG), a research and development program with regard to the hydrological performance of various covering systems is being carried out. For this purpose, six large-scale test fields with a size of 500 m² each have been built. All fields are designed as multilayered systems with a combination of topsoil, drainage layer and barrier system. Compacted clay liners, combined systems of flexible membrane liners on top of compacted clay layers and a combined system of compacted clay on top of a capillary barrier system are tested as barrier system variants on two different slopes. On these test fields, all discharges (surface run-off, interflow in topsoil and drainage layer and the leakage through the barrier systems), as well as soil hydrological and meteorological parameters, are measured.

The tests focus on the comparative evaluation of the long-term effectiveness of the different covering systems and on the physics of water movement within the different barrier systems. The measurements were started in the beginning of 1988. The first results show that up to now all systems perform better than required by regulations. The course of the discharges, collected below the barrier systems show a peak during the first months. This is interpreted as pore water outflow of the compacted clay layers due to consolidation. The best results are achieved by the extended capillary barrier systems, where even the pore water flow is drained off laterally so that there is no infiltration of water into the disposed waste.

INTRODUCTION

In the Federal Republic of Germany (FRG), about 45,000 abandoned waste disposal sites are suspected to cause contamination to the environment (1). About 2,400 of those sites are concentrated in the Hamburg industrial district. About 140 of those sites are suspected to have a high toxic potential. In most cases, the use of groundwater as drinking or irrigation water is threatened and require remedial action. Very often, highly toxic industrial waste has been mixed with municipal waste. Clean-up strategies, therefore, have to deal with large amounts of waste with a variable composition. In all those cases where excavation or in situ treatment are not available due to political, financial or technological limitations, the only remaining and at least temporarily efficient strategy is to isolate and drain the waste. Covering systems play a central role in those concepts.

Covering systems have to meet different requirements: (1) the system itself has to prevent infiltration of rainfall into the waste, enable a controlled gas collection, and often must be suitable for recultivation. In the long run, a cap must be resistant against loads and stresses like subsidence, erosion, biopenetration, desiccation and clogging of the drain system. (2) Evaluating not only the efficiency of the system itself but also the contamination risk of the whole site, the demand is that the covering system must be built as fast as possible. The more complicated it is to plan and to build a cap, the more rainfall will infiltrate the waste. (3) In general, a covering system must be cost-effective so that it enables the protection of as many sites as fast as possible with a given budget.

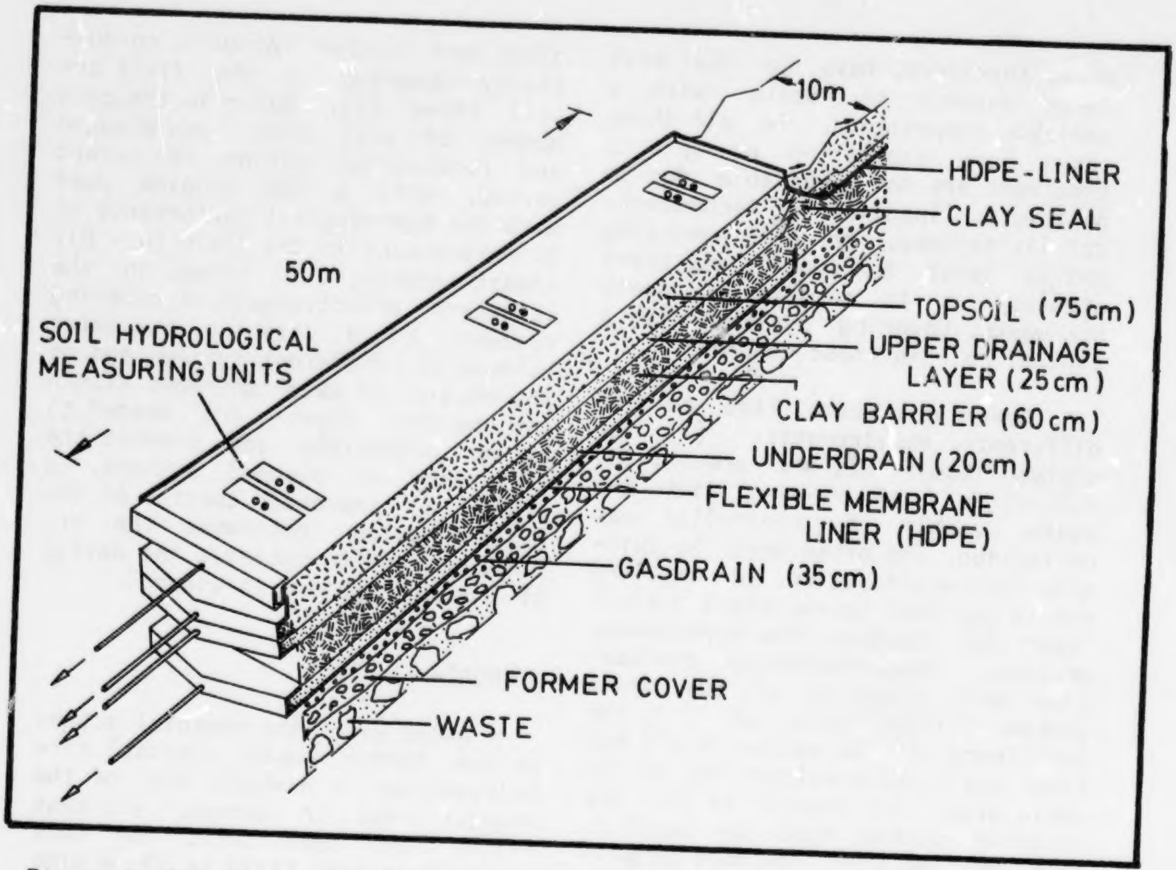
PURPOSE

Landfill caps usually are rather complex and expensive due to the requirements they have to meet as a system. In most cases, they are multilayered systems with a combination of topsoil, drainage layer and one or more barrier layers. A lot of information concerning the percolation of compacted clay liners have been derived from laboratory experiments (summary in 2). The differences between laboratory data and the often much higher hydraulic conductivity observed in the field are well known (3). But even though a number of caps have been planned and constructed during the recent period, only a few studies deal with the hydrological performance of different caps in the field (4 - 8). Almost nothing is known on the long-term effectiveness of covering systems. Field data on the water balance of different systems and on the physics of water movement within the barrier layers are needed to better understand and predict the efficiency of planned systems, to enable an improved control of the factors which determine the efficiency, and to optimize the design of covering systems in general.

APPROACH

Along with the remedial action on the former waste disposal site Georgswerder in Hamburg, one of the biggest sites in Europe, six test fields have been built for this study. Each test field is 10 m wide and 50 m long in slope direction (Fig. 1). The fields are integrated in the landfill cover, but flow from the high slope and lateral flow into the test fields are prevented by a combination of flexible membrane liners (HDPE) and clay seals. Therefore, each test field has its own water balance. Gravel-filled underdrains consisting of welded HDPE liners are installed below the barrier systems. They enable the collection and direct measurement of the barrier system leakage rates.

The test fields are located in two areas with different slope (F-fields with 4 %, S-fields with 20 % slope). The slope and design of the barrier system are varied in such a way that the influence of these factors on the water balance can be determined



10m
HDPE-LINER
CLAY SEAL
50m
SOIL HYDROLOGICAL MEASURING UNITS
TOPSOIL (75cm)
UPPER DRAINAGE LAYER (25cm)
CLAY BARRIER (60cm)
UNDERDRAIN (20cm)
FLEXIBLE MEMBRANE LINER (HDPE)
GASDRAIN (35cm)
FORMER COVER
WASTE

Figure 1. Schematic view on a test field.

separately (Fig. 2). All fields are designed as multilayer-systems with a combination of topsoil, drainage and barrier layers. Due to the comparative testing concept, the topsoil and the drainage layer of all fields are designed alike (75 cm of sandy loam respectively, 25 cm of fine gravel, separated by a geofabric to protect the drainage layer). The barrier systems vary as follows:

- A compacted clay liner on F1 and S1 (three lifts of glacial till, 60 cm thick).
- A combined barrier system composed of a welded flexible membrane liner (HDPE) on top of a compacted clay liner (F2 and S2, the clay liner has the same design as on F1 and S1). The quality of the HDPE liners has been thoroughly controlled during the construction. Therefore, they are assumed to be watertight during the first years of the study. During that time, these fields serve as control plots concerning the percolation of the barrier system and for that reason allow the precise detection of pore water discharge due to consolidation of the clay liners

after the installation of the upper drainage layer and topsoil.

- Standard design of the Georgswerder cover (F3). Like F2 and S2, HDPE liners, however, not welded but installed overlapping in slope direction on top of a compacted clay liner.
- Combined barrier system consisting of a compacted clay layer (40 cm thick), lying above a capillary barrier consisting of the capillary layer (60 cm, fine-grained sand) on top of the capillary block layer (25 cm, coarse sand/-fine-grained gravel, S3). In that extended capillary barrier design, the upper clay layer provides a low intensive infiltration into the capillary layer. Therefore, the capillary barrier can operate under unsaturated conditions using the wick effect even after heavy rainstorms or after melting of snow.

The measuring program covers the following range:

- The discharges (surface run-off, interflow in topsoil and drainage layer as well as leakage through the barrier system) are collected and measured individually and with high temporal resolution.
- In some fields, various soil hydrological measuring units with a total of 24 neutron probe tubes and 531 automatically recording tensiometers are installed (e.g., in Fig. 1) to define moisture content and hydraulic potential in high temporal and spatial resolution.
- A weather station serves to measure precipitation, air temperature, humidity, wind velocity, radiation balance and soil temperature to determine the water input by precipitation and all parameters necessary to compute evapotranspiration using the Penman/Monteith equation.

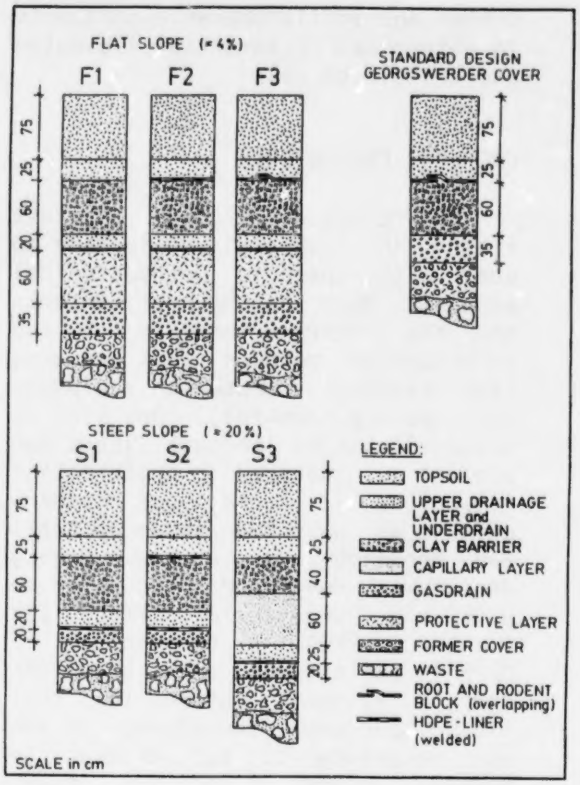

FLAT SLOPE (≈4%)
F1
F2
F3
STANDARD DESIGN GEORGSWERDER COVER
75
25
60
20
60
35
STEEP SLOPE (≈20%)
S1
S2
S3
40
2020
2025
LEGEND:
TOPSOIL
UPPER DRAINAGE LAYER and UNDERDRAIN
CLAY BARRIER
CAPILLARY LAYER
GASDRAIN
PROTECTIVE LAYER
FORMER COVER
WASTE
ROOT AND RODENT BLOCK (overlapping)
HDPE-LINER (welded)
SCALE in cm

Figure 2. Layer design of the test fields

In addition, several soil physical, chemical and mechanical parameters are analyzed in the laboratory or determined by additional experiments in the field: (e.g., grain-size and pore-size distribution, saturated and unsaturated hydraulic conductivity, bulk density, proctor density, plasticity, shear strength, clay mineralogical composition, inorganic constituents of the discharges, tracer and infiltrometer experiments to determine preferential flowpaths and transit times).

PROBLEMS ENCOUNTERED

Hydrological studies on test fields in technical scale have to deal with specific methodological problems such as boundary effects and the representativity of the construction methods that are used (for example, compaction equipment and quality control). Any kind of material cutting through liners can produce undesired preferential flowpaths. To avoid those boundary effects as have been shown by Hötzl and Wohnlich (9), a new boundary design was developed in cooperation with the engineering office IGB (Hamburg, FRG). A combination of HDPE liners and clay seals above the barrier systems define the test field boundary. Therefore, it was not necessary to cut through the barrier systems. In addition, it was possible to construct the clay liners of the test fields continuously over all fields with the same equipment, technique and quality control similar to the whole landfill cover.

A large number of technical problems had to be solved concerning construction details, measuring techniques and data collection which cannot be mentioned here in detail (e.g., leak-free construction of the pipes between test fields and measuring shafts in a way that allows subsidence; installation of instruments in the barrier systems without causing leaks; protection against lightning). Some new instruments have been developed (e.g., pressure transducer tensiometers, discharge measuring instruments). In general, the following strategies have proven to be very important: (1) a very close quality control with always at least one person at the site observing the construction progress; (2) a redundant measuring concept concerning instrumentation, data collection and independent verification of the data (the crucial data, for example, are all measured and registered on two independent ways, automatically and manual); (3) a modular setup of the instrumentation and easy-to-calibrate-instruments reduce interruptions of measurements and data collection due to technical defects.

Due to the bad weather conditions during the construction of the fields, the three flat fields were completed later than the steep fields. This resulted in slightly different initial soil water contents and germination conditions for the seeds. Therefore, the species composition of the vegetation is not totally similar on all fields (yet the type of vegetation, a short grassland with no shrubs and trees, is the same).

RESULTS

The research and development program was started in 1986. It took one year to plan the test fields and another year to build them. The measurements to determine the water balances of the fields (precipitation, discharges and soil water contents) started at the end of 1987. Therefore, only preliminary results can be given.

Looking at the measured discharges, the following phenomena can be described:

- There is surface run-off under both slope conditions, though frequency and intensity are higher on the S-fields (2.6 % of rainfall on the S-fields, 0.5 % on the F-fields). Only very little erosion occurred during the first winter even though there was almost no vegetation on the fields in that time.

- Lateral flow within the topsoil only occurs on the S-fields. It contributes only 0.8 % to the total balance.

- The widest range of flow intensities can be observed in the upper drain layers. There is only little effect of slope concerning the total volume of flow, but the flow intensity can be more than two times higher on the steep slope.

- Fig. 3 shows the amounts of water that have been collected below the different barrier systems. The measurements started during construction, which ended on the steep fields in week No. 40 and on the flat fields in week No. 48. In Fig. 3a and 3b, the flow rates on the fields S2 and F2 with a combination of HDPE and clay liners are compared with the flow rates of the respective fields S1 and F1 with just clay liners. Considering the HDPE liners on S2 and F2 as impermeable, the black bars show the pore water flow out of the compacted clay liners due to consolidation during and after the construction of drainage layer and topsoil. The white bars give the sum of pore water flow and leakage through the clay liners of S1 and F1.

In general, the data show a low intensity of flow. There is a significant pore water discharge during the construction of the topsoil. The flow decreases in the following weeks, but one year later, still exists. No change in

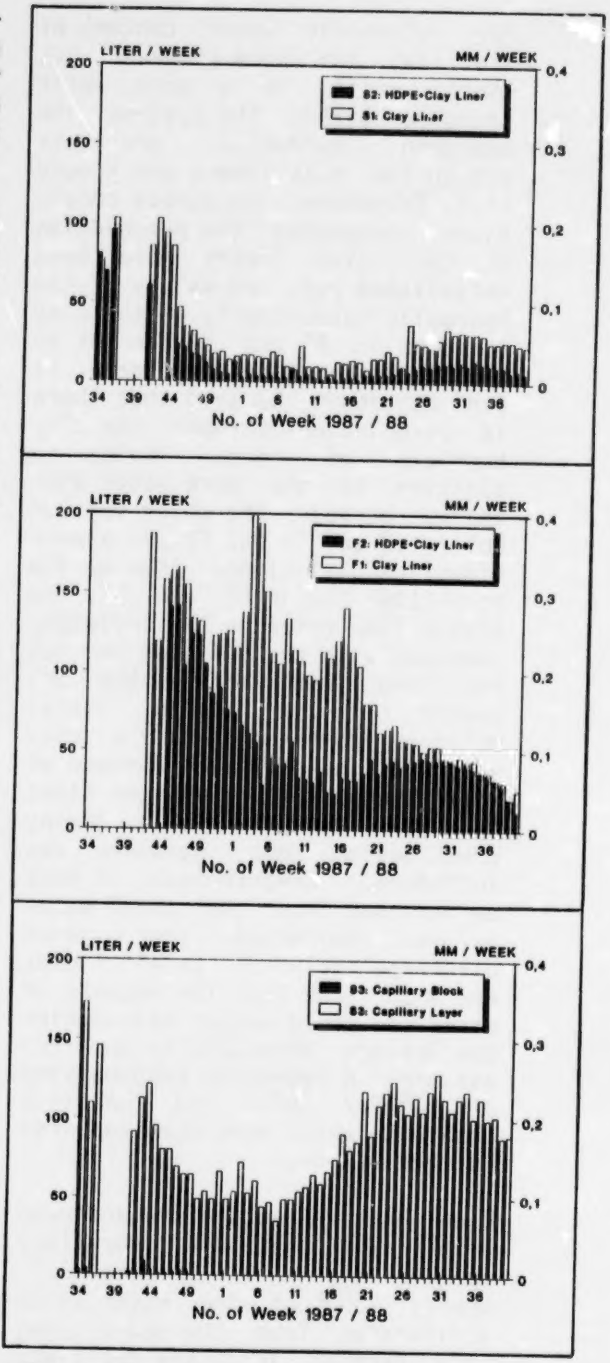


Figure 3. Water collected below the different barrier systems in liters and millimeters per week

the volumetric water content of the clay has been observed, but there still is a pore water pressure within the systems. The measured hydraulic gradients within the clay liners are around +1.8. Therefore, no steady conditions concerning the percolation of the clay liners have been established yet, and values of the hydraulic conductivity of the clay barriers on F1 and S1 can not be calculated based on these data. It can at least be said that there is percolation through the clay barriers of these fields in addition to the pore water discharge because the water volumes collected on F1 and S1 are always significantly higher than on the respective fields F2 and S2. The higher flow rates on the F-fields, compared with the S-fields are not resulting from slope, but are caused by the higher initial moisture contents of the clay layers of these fields. Because of different weather conditions (that is i.e., more rainfall) during construction more moisture was introduced. Nevertheless, it must be stressed that the total water volumes collected (pore water discharge included) on all fields are much less than the amounts of water one would expect calculating the leakage through clay barriers assuming a hydraulic conductivity of 1*10-9 m/s and realistic gradients which have been required by regulations.

Even better results are achieved with the extended capillary barrier system on S3 (Fig. 3c). Nearly 100% of the water which infiltrates from the above lying clay barrier into the capillary layer moves laterally within the fine sand and does not pass through the capillary barrier.

Up to now, all systems are working satisfactorily. Further measurements will show how the systems perform on a long-term basis. On sites where suitable materials are available nearby, the extended capillary barrier might be the best and most cost-effective type of cap. Further work will deal with the maximum drainage length, the influence of slope, vapour movement and material properties on those systems. A more detailed interpretation of the data of the Georgswerder test fields showing the water balances, response times of the different discharges to rainfall events, and of the spatial variability of the soil properties measured during construction is in progress.

ACKNOWLEDGEMENTS

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Disclaimer

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DESIGN AND CONSTRUCTION OF THE C2-LANDFILL MAASVLAKTE ROTTERDAM

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ABSTRACT

By assignment of the AVR Chemie C.V. Rotterdam Public Works started in 1985 with a design of the C2-Landfill for non-treatable chemical waste of the so-called middle class (C2). The disposal is under construction now. The chemical waste will be stored above ground level on the Maasvlakte in Rotterdam. The Maasvlakte was created by hydraulic sand filling of an in part of the Haringvliet estuary. The landfill consists of a concrete basin with a volume of 210.000 m3. The dimensions are 50 x 320 x 11 m, the concrete surfaces of the walls are protected with a HDPE liner. The bottom liner consists of a layer of 100 mm of cast-asphalt and a crack-bridging membrane which provides a high degree of safety. A drainage system in and under the basin will be made for transport and control of the leachate.

After the C2-landfill is filled completely it will be covered with a final layer of two HDPE liners with a bentonite-clay liner in between. On top of this cover and the concrete basin a sand layer will be applied, so that a dune is created.

INTRODUCTION

In the Netherlands there are at present too few possibilities to dispose of non-treatable chemical wastes in a sensible, environmentally hygienic manner. The major part of this type of waste is now transported to land- fills abroad. The rest must be stored where it is produced. In 1984 the Dutch government, the municipality of Rotterdam and eight large industrial companies established the AVR Chemie C.V. The storage site for non-treatable wastes is an essential component of this company.

Government policy on chemical waste is based on prevention of the production of such waste and promotion of its re-use. It is anticipated that modification of production methods, new treatment technics and re-use will lead to a reduction of the stream of untreatable chemical wastes. Therefore the C2-landfill is intended to receive C2-waste for the coming ten years.

PURPOSE

Because storage of C2-chemical waste at producers' sites involves an environmental risk, spreading of such storage activities criss-cross over the country must be avoided. Therefore a storage of nontreatable waste is necessary by building and operating a secure landfill at a place that has no consequences to the environment. To this purpose the landfill is situated above ground level.

APPROACH

To build a C2-landfill facility, a number of permits are required. When decisions have to be made on environmental licenses, it is important to have a good idea of the consequences of a C2-landfill to the environment beforehand. The present Environmental Impact Statement (EIS) has been drawn up to aid decision making on:

- dispensation under the Dutch Chemical Waste Act;
- the Nuisance Act license;
- the Discharge license in pursuance of the Pollution of Surface Waters Act.

This EIS will be open to inspection when the requests for these licenses are submitted, and will be discussed during a public hearing. Only after this, and after assessment of possible objections that are submitted, will a decision be taken about the requests for licenses.

Some important features for making the design of the C2-landfill are:

- only non-treatable chemical waste of the so-called middle class (C2);
- compartimentation;
- capacity 210.000 m3;
- filling period about 10 years;
- the waste cannot be driven over due to high moisture content and low stability;
- the leachate and percolate seepage must have been expelled within a period of 30 years;
- a control and securety system under the basin to monitor ground water pollution;
- a final minimum distance of 0.50 m between the foot of the chemical waste and the ground water;
- a maximum permissible crack width is fixed at 0,2 mm;
- free rain water penetration in the C2-waste must be avoided by movable roofs;
- final cover after filling which prevents rain water to penetrate the waste;
- a sand layer will be applied, so that a dune is created;
- a suitable location.

DESIGN AND CONSTRUCTION

C2-waste

Non-treatable chemical wastes are divided into a number of classes, depending on the quantities in which they are produced, the treatment possibilities and the environmental hygiene considerations.
Chemical wastes which may only be deposited above ground under special regulations and special provisions are considered to belong to the C2-class.
Examples are:

- metal sludge.
  Originates mainly from the treat-

ment of wastewater from electro plating and engraving plants. It contains various heavy metals and other components.

- Leather tanning sludge.
  Originates from the treatment of wastewater from leather tanning plants. Chrome is the main contaminant.
- Gas scrubber sludge.
  Originates from incineration of, among others, chemical waste. It contains various heavy metals.

It is estimated that 25,000 - 30,000 tons of C2-waste per annum will be deposited in the landfill.

Situation

The landfill is situated on the Maasvlakte Rotterdam. The choice of a site on the Maasvlakte, was mainly based on the compatibility with the landscape, the future use that would be made of the area, the timely availability of a site and the stable subsoil.

Settlements and ground water levels

The calculation of settlements has been based on soundings carried out in the area. The total settlement of the lower side of the basin has been calculated at 0.50 m. The highest ground water level (1 x 10 years) during the dumping phase will be approx. NAP +4.00 m. A horizontal drainage system round the C2-landfill will prevent further extreme rises in the ground water.

Taking account of the settlements (0.50 m), sinking of the ground and rising of the sea level (0.10 m) and the capillary head of the ground water (0.10 m), the foot of the chemical waste should be at NAP +5.20 m (during initial period), in order to achieve a final minimum distance of 0.50 m between water and waste.

Capacity

The chemical waste will be stored above ground level in a reinforced concrete basin with a volume of 210.000 m3. This volume will probably be enough for 5 to 10 years of use. A cross-section is given in, figure 1.

Compartimentation

The basin is divided in two main sections separated by a (vertical) concrete wall. In the smaller section all wastes containing more than 2% by weight of lead, chromium, copper and nickel will be deposited. This section (above 15% of the total capacity) is aimed at waste with a potential for re-use in the (near) future. In the main section all other middle-class waste stream will be disposited. The sections are presented, in figure 2 (lay out).

Design criteria

The basin is constructed of reinforcement concrete executed in accordance with the VB 1984 (Regulations for concrete) as watertight concrete. The materials used are: blast furnace cement class A, with a slag content 65% and reinforcement steel Feb 400 HW quality with a yield strength of 400 N/mm2. The cover has to be 50 mm minimally. The materials mentioned have been chosen to obtain the greatest possible watertightness of the concrete and the highest guarantee for the durability of the structure (about 150 years).

Reinforced concrete always shows cracking. For the greatest possible watertightness it is important to limit the width of the cracks as much as possible. For this reason a maximum permissible crack width of 0.2 mm is taken for designing the reinforcement. The calculation and design of the structure with the aid of the computer program DIANA, is further based on a safety factor of 1.7 in relation to the ultimate limit state (failure). A concrete structure always shows cracking. This is the reason why the Authorities that give the permits take the view that the waste can be in direct contact with the ground-water.

In a risk analyses it is supposed that the concrete structure is not watertight, due to which the sealing of the basin (HDPE liner and cast asphalt) must supply the watertightness. In practice the concrete structure can be considered as watertight (mixture of the concrete, thickness of the floor and walls and the crack width requirement). In the construction phase, measures are taken to allow the shrinkage of the concrete due to temperature and hardening process to take place freely. If this is not done, uncontrolled cracking in the structure could result. The concrete floor construction, which is made without expansion joints is therefore provided with a series of shrinkage strips. The joints in the concrete floor will be made later on, so shrinkage is limited. Cracks that possibly develop during the construction phase will be injected with epoxy-resin. The concrete walls are made with expansion joints every 40 m. The joint strip is made of HDPE.

Innerliner

The concrete walls are protected with a 2 mm thick HDPE liner. The HDPE liner is prefabricated in length of 11 m and 1.40 m widths and welded on vertical HDPE-strips embedded in the concrete. So a continuous connection between liner and concrete is obtained.

Bottom liner

The general functional requirement for the bottom liner is, that it must form a "moisture proof" barrier between the landfill and the environment for at least the period of drainage (30 years at minimum). The bottom liner consists of a crack-bridging rubber bitumen membrane and cast-asphalt layer. The membrane must prevent cracks in the concrete floor to extend into the cast-asphalt layer. The asphalt layer approx. 100 mm thick, forms the sealing layer. The chemical resistance to the leachate should be such that the chance of emission in the dewatering phase, is at an acceptable level.

Solvents and oil products in sufficiently high concentrations attack bitumen. The most extreme and safest approach is to assume that the total amount of solvent in a mixture of solvent is absorbed into the bitumen. Then 10 mg/l will be taken as maximum summed concentration of solvents in both leachate and percolate. No account is taken of the fact that the leachate-percolate is continuously pumped up and transported to a storage basin and that evaporation of the solvent will occur.

It is known from research on bitumen by the Royal Shell laboratory Amsterdam that up to a concentration of 100 mg/l the mechanical properties of the bitumen do not change.

Drainage system in the basin

On the asphalt layer a 0.75 m thick drainlayer is constructed consisting of coarse sand. This layer contains a drainage system of

HDPE pipes. Valves in these drain pipes make it possible, that during the filling phase the leachate-percolate and clean rain water are seperated. The leachate-percolate and the clean water shall be continuously pumped up and stored in a reservoir for leachate-percolate and in a reservoir for clean water.

Drainage and security system under the basin

The soil under the concrete basin will be divided in 5 separate soil compartments by HDPE synthetic walls. In each section a drainage system is constructed so that monitoring of leakage to the ground water is possible. If, due to a possible leak in the bottom liner the ground-water under the basin is polluted, each section can be drained and sampled separately. By pumping on this system, the ground-water level under the structure will be lower than the surrounding ground-water level, so the effect of the pollution will be limited to an area immediately below the landfill. All systems of drainage in, as well as under the basin ends in 4 vertical shafts. Leachate-percolate and clean water are pumped from these shafts to the reservoirs.

Portal crane

Because the C2-waste due to high moisture contents and low stability cannot be driven over by trucks, the filling is done by a portal crane with a span of approx. 50 m. This crane runs on rails along the length of the concrete basin. A road is constructed on the soil embankments beside the basin. The crane is semi-automatic and can dump the C2-waste in a network of 3 x 3 m2 and the time, the place and specification of the C2-waste are registered by computer automatically.

Movable roofs

During the filling phase, the dumping front must be protected against penetration of rain water. Because one of the requirements is that the leachate-percolate seepage muste have been expelled within a period of 30 years, free precipitation on the waste would be contrary to this requirement. The requirement can be met by using movable roofs. The slope of the waste is estimated to be about 15° and so has a length of about 50 m.

Two roofs elements of 22 x 50 m are necessary for the smaller section and two roofs elements of 29 x 50 m for the main section. A rail construction is laid of both long sides of the concrete basin.

Leachate-percolate basin

The leachate-percolate is collected in the leachate basin. This structure is made by two HDPE liners with a sandlayer in between. The drain layer is provided with an observation well which functions as a leakage detector. To avoid filling with rain water, a tentlike roof structure is laid over the basin. To cope with possible stagnation of the leachate transport, the basin has a volume of 300 m3 equivalent to the amount of leachate and relevant waste water occurring in at least two months.

Clean water basin

Non-polluted water is collected in the clean water basin. The basin is sunk in the ground and consists of a single HDPE sheet. To reduce the pump capacity of the pumping station the basin has a content of 100 m3. The clean water is discharged into the Mississippi Harbour by pressure pipe.

Monitoring system

Minimally six observation wells are to be placed round the C2-landfill. One by each shaft, as these are places with a relatively higher risk, and one at each narrow side. The leachate basin may be a place with higher risk potential. Two observation wells will be placed near the leachate basin.

Permanent cover

When applying the cover system, account is taken of the settlements occuring in the waste fill. These settlements will occur especially in the filling phase. For this reason the final cover system will only be applied about two years after completion of the filling. In the intermediate period a temporary liner will be laid. The final cover consists of two layers of HDPE liner with a bentonite-clay liner in between. On top of this cover and the concrete basin, a sand layer will be applied so that a dune is created. The proposed design incorporates a cover system with a limited lifetime, so that regular inspection will be necessary.

COST AND PLANNING

The cost of investment of the C2-landfill are about Dfl. 34.000.000.-- and will be payed by the Dutch government. The running cost are for the AVR Chemie C.V.

The construction activities started in the beginning of 1988. The landfill will be in operation at December 1989.

CONCLUSIONS

By realising the secure landfill for non-treatable chemical waste in the Netherlands, a storage is possible in a sensible and environmental hygienic manner. Especially for the small producers of such waste, this site is important.

At the same time a program must be started for treating chemical waste so that the stream of waste will be reduced to acceptable proportions in future.

Disclaimer

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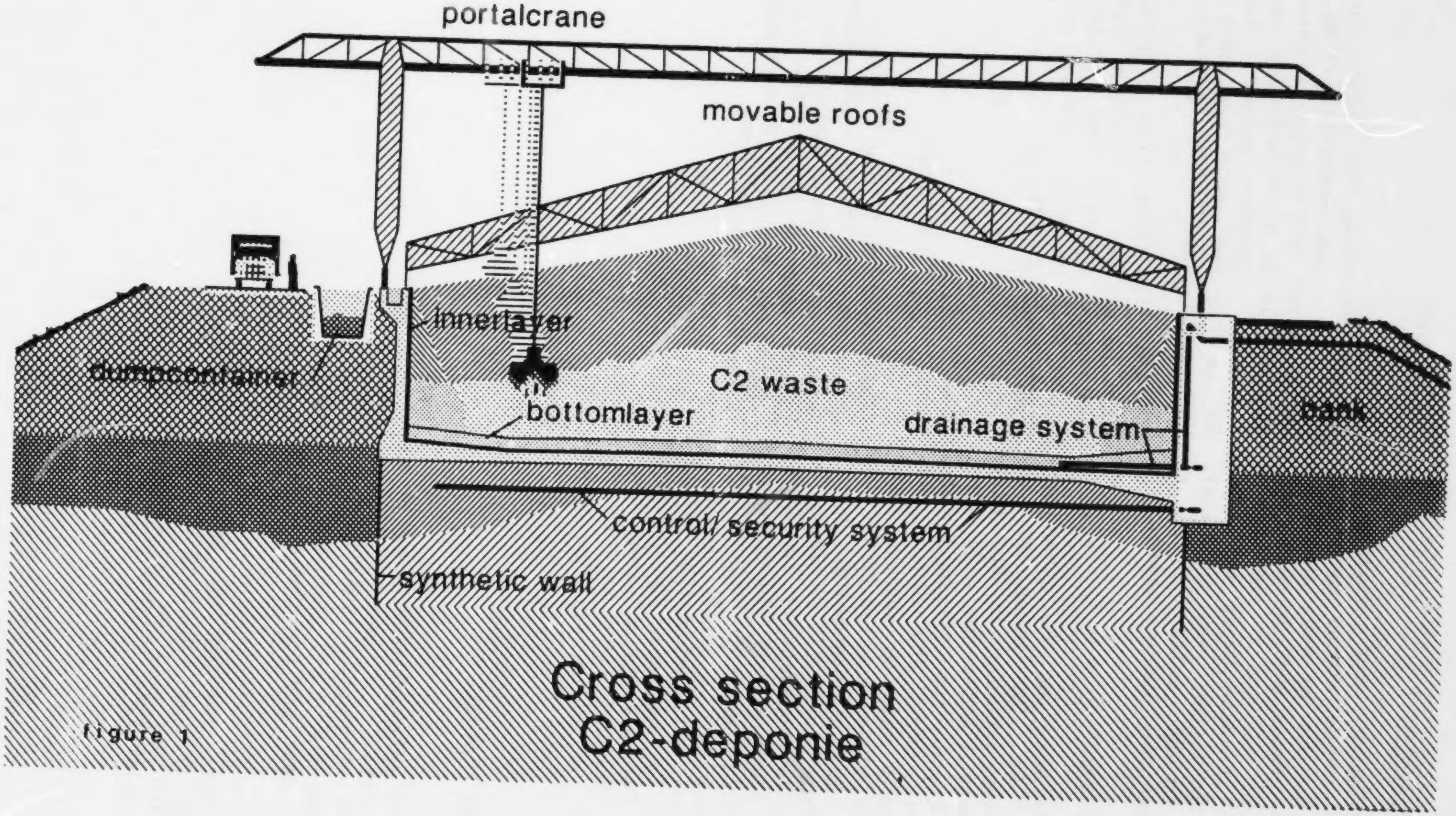
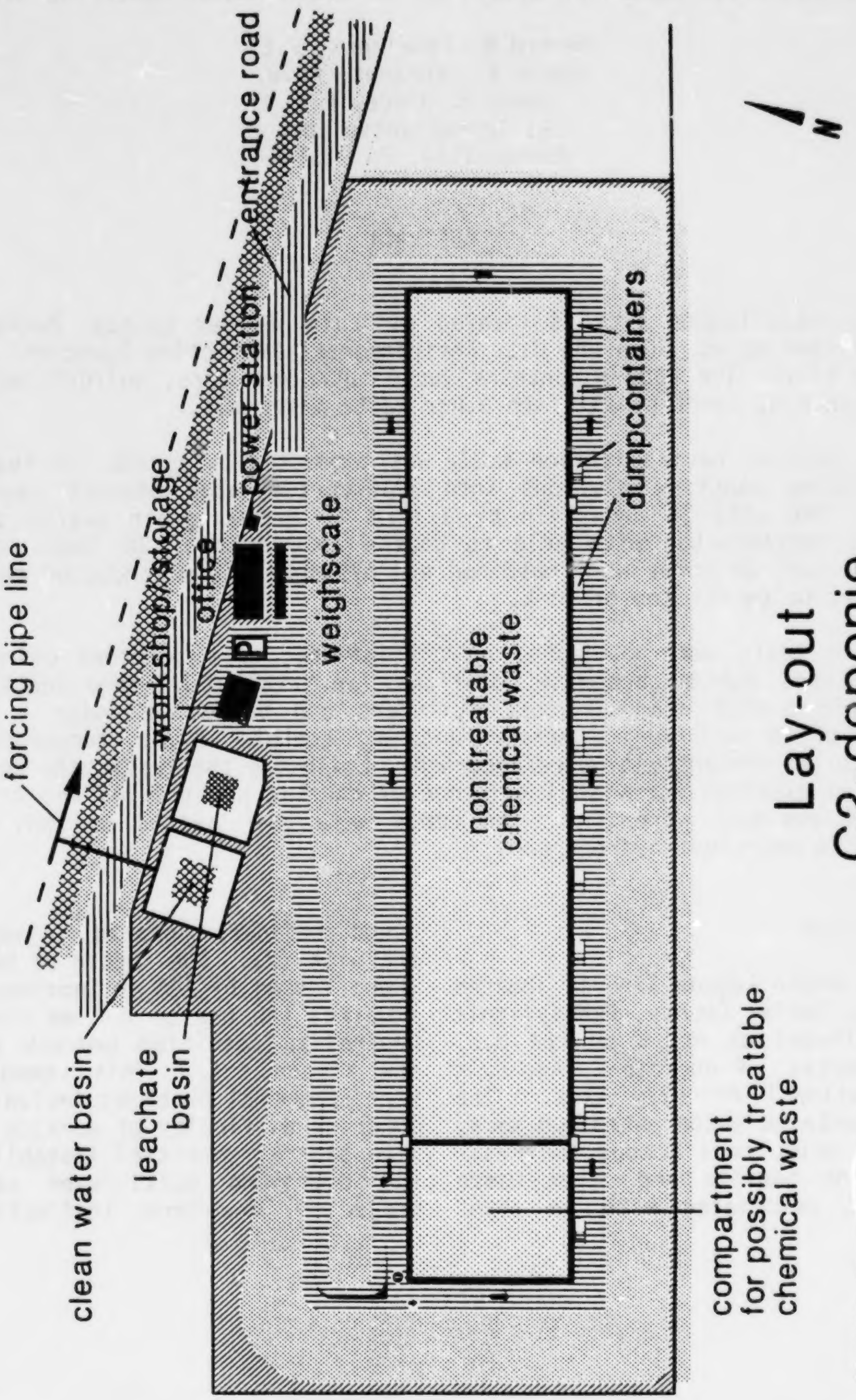

portalcrane
movable roofs
innerlayer
dumpcontainer
C2 waste
bottomlayer
drainage system
bank
control/ security system
synthetic wall

Cross section
C2-deponie

figure 1


forcing pipe line
workshop/storage
office
power station
entrance road
P
weighscale
non treatable
chemical waste
dumpcontainers
clean water basin
leachate
basin
compartment
for possibly treatable
chemical waste
N

Lay-out
C2-deponie

figure 2

BEDROCK NEUTRALIZATION STUDY FOR THE BRUIN LAGOON SUPERFUND SITE

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ABSTRACT

The Bruin Lagoon site is located in Bruin, Butler County, Pennsylvania, and is listed as No. 3 on the U.S. Environmental Protection Agencies' National Priority List. The Lagoon contains waste petroleum tars, sulfuric acid, coal combustion ash, spent bauxite and other waste materials.

The bedrock neutralization study was conducted to assess the feasibility of injecting caustic solutions into acid-contaminated bedrock beneath the lagoon. The site is underlain by a fine to medium grain quartz sandstone which is contaminated with acid to depths in excess of 30 feet. For this investigation, Nx-cores were obtained and pressure tests conducted to a depth of 30 feet below the top of rock.

Leach tests were conducted on contaminated core sections using sodium hydroxide and sodium carbonate solutions. A total of 12 core sections were exposed in 3-inch diameter test cylinders and permeated under a positive pressure of 25 to 50 psi. Measurements of leachate volume, temperature, pH, and hydraulic conductivity were recorded. Following the tests, the cores were split, and examined for visual evidence of caustic penetration and crushed to determine residual strength. The cores were then tested for pH, TOC and extractable petroleum hydrocarbons.

INTRODUCTION

The Bruin Lagoon Site is located in Bruin, Butler County, Pennsylvania and is listed as No. 3 on the U.S. Environmental Protection Agency's (EPA) National Priority List. The lagoon contains waste petroleum tars, sulfuric acid, coal combustion residue, spent bauxite and other waste materials associated with an abandoned refinery located adjacent to the site (2). The Record of Decision (ROD) issued by EPA in September 1987 required the use of a lime slurry to neutralize acidified bedrock beneath the lagoon (3). This remedy presented several problems including the inherent difficulty of working with a lime slurry, potential instability to the overlying multi-layer cap and projected long-term ineffectiveness of the treatment. As a result, GAI Consultants, Inc. (GAI) proposed to perform a laboratory study to evaluate alternative methods of neutralizing the bedrock.

PURPOSE

The bedrock neutralization study was conducted to assess the feasibility of caustic solution injection as an alternative for the treatment of the acid contaminated bedrock beneath the lagoon. The program included field measurements of bedrock permeability and laboratory rock column tests to determine the effectiveness of several alkaline treatments.

APPROACH

Rock cores obtained at the Bruin Lagoon indicate that the site is underlain by a fine to medium grain quartz sandstone. Cores were obtained to a depth of between 25 to 30 feet below the sludge/rock interface. The upper 5 feet of the rock section tends to be very broken to broken, black to dark gray in color, and impregnated by sludge in both pores and fractures. At increasing depth, the rock becomes broken to massive and grades to a light gray color with natural, black carbonized laminae that are oriented at between 15 and 35 degrees. Angular fractures oriented at between 20 to 90 degrees typically exhibited iron staining with black tar-like residue on some fracture faces to a depth of 20 feet beneath the rock interface. Measured pH values of between 1.2 and 1.7 were recorded in the upper 5 feet of the core sections with pH values of between 2.7 and 6.2 recorded at the bottom of the core sections (1).

Hydraulic pressure tests were performed in 4 of the 5 core holes. Measured bulk rock permeabilities varied between $1\text{x}10^{-3}$ and $5\text{x}10^{-6}$ cm/sec with higher permeabilities controlled by rock fracturing. In general, the effect of pore and fracture clogging by translocated sludge material is reflected in the lower permeabilities ($2.2\text{x}10^{-5}$ to $<4.9\text{x}10^{-6}$ cm/sec) measured in the upper 5 feet of the core-hole sections. Similar permeability values were calculated for rock core sections permeated in the rock column tests.

Bedrock neutralization tests were performed on select core sections using sodium hydroxide and sodium carbonate solutions. Tests were performed on individual core sections using 0.01, 0.1, 1.0 and 10 normal sodium hydroxide solutions and 0.1 and 1.0 normal sodium carbonate solutions. A total of twelve (12), 2-inch thick Nx-core sections were epoxied into 3-inch diameter, schedule 80 test cylinders with threaded end caps and drainage ports. After sufficient setting time, the rock sections were tested for leaks, sealed and placed in a protective outer casing, and leached under a positive pressure (25 to 50 psi) until 125 milliliters of test solution (approximately 8 pore volumes) had passed through each core section.

During testing, measurements of leachate volume, temperature and pH were recorded. Following leaching the core sections were removed from the test cylinder, split axially and examined visually for signs of caustic leaching. The core sections were then tested for unconfined compressive strength and crushed for chemical analysis. Chemical analyses performed on the crushed core samples included pH (SW-9045), total organic carbon (Walkley-Black) and total recoverable hydrocarbon (EPA 418.1). Representative sections of untreated rock core were also tested and analyzed to define baseline conditions.

PROBLEMS ENCOUNTERED

A 10 N sodium carbonate solution was used in several column tests, but failed to permeate the rock samples due to crystal formation and precipitation on the upper rock surface. No other significant problems were encountered in conducting the study.

RESULTS

Column test data for rock specimens are summarized in Tables 1 and 2. The core sections were permeated with a weak base solution (sodium carbonate) and a strong base solution (sodium hydroxide). In each instance, the resulting leachate was noticeably darkened indicating leaching of the impregnated sludge (hydrocarbons) from the rock cores (Table 2). The effects of contaminant removal were particularly evident in visual comparisons of axial core fractures with the treated cores demonstrating a lighter coloration characteristic of the uncontaminated quartzitic sandstone. Leaching of the cores using both test solutions also produced a significant reduction in the unconfined compressive strength of the rock (Table 2). This result may be due to the selective removal of natural binding agents and/or interstitial sludge which may have held sand grains together in the untreated sample.

During performance of the tests, leachate volumes were recorded and subsequently used to calculate rock permeabilities. Permeabilities of the sludge impregnated core samples were found to vary between $6.9\text{x}10^{-5}$ and $4.4\text{x}10^{-6}$ cm/sec in conformance with field permeability results. In general, lower permeability valves were measured for rock samples from the 409 core series, a finer grain sandstone, which appeared to be more heavily impregnated with sludge and provided low pH values. Measurements of test solution pH before leaching and after permeation of the core sections indicate that the sodium carbonate solutions (0.1 and 1.0 N) were readily acidified by the contaminated rock samples (Table 2). In contrast, the sodium hydroxide solution (0.1 to 10 N) showed no significant alteration of effluent pH except at low solute concentrations (Table 2).

These results and the corresponding rock pH values before and after treatment (Table 2) confirm that use of a weak base would be ineffective in treating the acidic bedrock. It was further determined that use of a 0.01 to 0.1 normal sodium hydroxide solution would be effective in treating the rock beneath the lagoon. Chemical reactions between the acid contaminated rock and caustic permeate were not observed during testing, nor was there any measureable back-pressure build up within the test cells after 24 hours as a result of gas formation.

Several alternatives were considered for neutralizing the acidic bedrock condition which has been documented to extend 20 to 30 feet beneath the site. The most effective option combines pressure injection of a caustic solution followed by pressure grouting using a high pH cement. The injected caustic solution would neutralize readily accessible acidity in surrounding rock pores and fractures, while

Table 1. Column Test Readings Bedrock Neutralization Study

Date	Time	Wt (min)	Pressure (psi)	Leach Vol (ml)	Pore Vol (Approx)	Temp (°F)	pH	K (cm/sec)
Column Test Using NaOH								
Core Test No. 109 A: Soln. Conc. = 0.1 N								
02-29-88	1200	0	25	0	0			
02-29-88	1230	30	25	10	0.7	68	-	-
02-29-88	1300	60	25	15	1.0	68	-	1.7×10^{-5}
02-29-88	1345	105	30	20	1.3	-	-	-
02-29-88	1430	150	30	60	4.0	-	-	-
02-29-88	1500	180	30	80	5.4	63	13.5	-
02-29-88	1600	240	30	125	8.3	58	13.5	3.2×10^{-5}
Core Test No. 109 B: Soln. Conc. = 1.0 N								
02-29-88	1100	0	25	0	0	68	-	-
02-29-88	1200	60	25	10	0.7	-	13.7	-
02-29-88	1230	90	25	80	5.4	68	13.8	-
02-29-88	1300	120	25	125	8.3	68	13.8	6.9×10^{-5}
Core Test No. 109 C: Soln. Conc. = 10 N								
02-29-88	1345	0	30	0	0	68	-	-
02-29-88	1500	75	30	10	0.7	63	12.0	-
02-29-88	1630	165	30	15	1.0	-	-	4.7×10^{-6}
02-29-88	1800	255	40	30	2.0	-	-	-
03-01-88	1000	1215	40	125	8.3	63	12.0	4.5×10^{-6}
Core Test No. 109 D: Soln. Conc. = 0.01 N								
04-12-88	900	0	15	0	0	65	-	-
04-12-88	910	10	15	25	1.7	-	3.1	-
04-12-88	950	50	15	40	2.6	-	3.7	-
04-12-88	1035	95	15	60	4.0	-	4.2	-
04-12-88	1245	225	15	125	8.3	-	5.2	5.8×10^{-5}
Column Test Using $NaCO_3$								
Core Test No. 409 A: Soln. Conc. = 0.1 N								
03-03-88	1100	0	20	0	0	-	-	-
03-03-88	1300	120	20	10	0.7	-	-	-
03-03-88	1400	180	20	15	1.0	-	-	5.5×10^{-6}
03-03-88	1500	240	30	20	1.3	-	-	-
03-04-88	930	1350	30	125	8.3	68	0.4	4.9×10^{-6}

(continued)

Table 1. (Continued)

Column Test Using $NaCO_3$

Date	Time	Wt (min)	Pressure (psi)	Leach Vol (ml)	Pore Vol (Approx)	Temp (°F)	pH	K (cm/sec)
Core Test No. 409 B:	Soln. Conc. = 1.0 N							
03-03-88	1100	0	25	0	0	-	-	-
03-03-88	1300	120	25	20	1.4	-	-	-
03-03-88	1400	180	25	25	1.7	-	-	9.2×10^{-6}
03-03-88	1430	210	30	30	2.0	-	-	-
03-03-88	1500	240	30	35	2.3	-	-	-
03-04-88	930	1350	30	125	8.3	68	4.1	4.4×10^{-6}
Core Test No. 409 C:	Soln. Conc. = 1.0 N							
03-03-88	1500	0	30	0	0	-	-	-
03-04-88	1030	1170	30	60	4.0	-	-	-
03-04-88	1200	1260	30	68	4.5	-	-	-
03-04-88	1330	1350	50	75	5.0	-	-	-
03-04-88	1500	1440	50	100	6.7	-	-	-
03-07-88	1000	1440	50	100	6.7	-	-	-
03-07-88	1100	1500	50	105	7.0	71	0.9	-
03-07-88	1200	1560	50	115	7.7	-	-	-
03-07-88	1230	1590	50	125	8.3	71	0.5	6.0×10^{-6}

pressure grouting of fractures would provide a long-term neutralization capability for remaining acidity at greater distance from the injection point.

Pressure injection of the caustic solution would be implemented in vertical increments within a network of closely spaced borings (Z 20 feet) followed by pressure grouting of open boreholes. Additional containment of the underlying bedrock contamination could be ensured by a peripheral grout curtain composed of acid resistant silicate grout mixture.

Pressure injection was determined not to be a cost effective solution at this site by U.S. EPA. Since the rock directly beneath the sludge can be considered almost impermeable as demonstrated in the previous section, the effectiveness of any caustic material placed directly on top of the rock will be severely limited. In addition, the multi-layer cap will be virtually impermeable to downward migration of gravitational water. Therefore, a layer of crushed limestone supplemented with agricultural lime was used in place of the lime slurry concept in the remedial design. This procedure will eliminate the problems associated with the lime slurry while providing long-term neutralizing capacity.

Table 2. Summary Bedrock Neutralization Data

Test Core No.	pH Leachate Test Soln.	pH Leachate Final Extract	pH Rock Before Leach	pH Rock After Leach	TOC (mg/kg)	Extractable Petroleum Hydrocarbon (mg/kg)	Crushing Strength (psi)	Core Permeability (k_{av} in cm/s)	Core Description
1. NaOH Treatment									
o 109 Untreated	-	-	1.7	2.5	5,100	<20	1,432	-	Dark gray, sludge impregnated, medium hard, medium grain quartz sandstone. 109 A through D series from upper 1.5' of core run.
o 109A (0.1 N)	13.8	13.5	1.7	9.7	320	<20	293	2.5×10^{-5}	Noticeably leached to light gray color, not as hard as untreated core sample.
o 109B (1.0 N)	13.8	13.8	1.7	10.2	950	<20	219	6.9×10^{-5}	Noticeably leached to light gray color, not as hard as untreated core sample.
o 109C (10 N)	11.8	12.0	1.7	12.8	2,400	<20	228	4.6×10^{-6}	Leached to light yellowish brown color (possible chemical reaction with mineral grains or waste material), not as hard as untreated core.
o 109D (0.01 N)	12.1	5.2	1.7	5.6	-	-	654	5.8×10^{-5}	Lighter grey color. Core section not as contaminated as Series A to C.
2. $NaCO_3$ Treatment									
o 409 untreated	-	-	1.3	1.3	4,100	600	1,262	-	Black, sludge impregnated, medium hard, fine to medium grain quartz sandstone.
o 409A (0.1 N)	12.2	0.4	1.3	3.5	2,400	<20	217	5.2×10^{-6}	Noticeably leached to medium gray color, not as hard as untreated core sample.
o 409B (1.0 N)	12.8	4.1	1.3	5.5	2,700	580	283	6.8×10^{-6}	Leached to light gray color with yellowish brown hue. Not as hard as untreated core sample.
o 409C (1.0 N)	12.8	0.5	1.3	10.0	3,500	<20	130	6.0×10^{-6}	Leached to yellowish brown color (possible chemical reaction wtih mineral grains or waste). Not as hard as untreated core sample.

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MODELING CHEMICAL AND PHYSICAL PROCESSES IN LEACHING SOLIDIFIED WASTES

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ABSTRACT

Solidification is an important treatment process in hazardous waste management and will continue to be so until waste minimization and waste recycle processes are perfected for all hazardous wastes. It is generally recognized that immobilization of contaminants in solidified wastes occurs through both physical and chemical mechanisms. Standard techniques for analyzing contaminant leaching measure only an observed diffusivity that does not separate chemical and physical factors. The suitability of the standard data analysis procedure is reviewed and alternative models developed that describe the separate effects of chemical and physical processes. These models describe physical transport through a solidified waste matrix according to Fick's law. Chemical reactions of sorption/desorption and precipitation/ dissolution are described. The observed diffusivity that would be calculated by ignoring chemical processes is shown to depend on the true effective diffusivity and coefficients that describe the chemical phenomena.

INTRODUCTION

Solidification is an important process for treating hazardous wastes and should become increasingly important in the future. Many wastes such as those containing inorganic contaminants cannot be destroyed by treatment nor can their production be avoided. Even wastes that are primarily organic and can be destroyed by processes such as incineration or chemical oxidation, often produce inorganic residuals that must be disposed. Until recovery processes are greatly improved, many wastes that contain toxic inorganic chemicals will continue to be disposed on or above land. Therefore, solidification processes that immobilize hazardous components of these wastes are essential to sound environmental management of these wastes.

Immobilization by solidification is generally considered to occur by two mechanisms. Physical processes operate by either immobilizing a contaminant completely by entrapping it in a solid matrix, or reducing its mobility by reducing the area through with it can migrate. Chemical processes can reduce mobility by converting the contaminant to a less mobile, or completely immobile form. Precipitation is an example of a chemical process that converts the contaminant to an immobile solid, and sorption is an example of a process that reduces the contaminant's mobility by fixing it onto the solid matrix.

Quantification of the degree of immobilization achieved by solidification processes is typically done by conducting leach tests. Results of these tests are usually interpreted in terms of a simple leaching model.[1-7] Leaching models can also be used to predict long term performance of the solidified waste material in the environment. As demands are made on solidification processes to provide a greater degree of immobilization for a wider range of contaminants, models will be expected to provide more information about the performance of these processes in order to aid in formulating further modifications.

PURPOSE

The purpose of this paper is to review and evaluate the standard model used to interpret results of leaching tests of solidified hazardous wastes, and to examine its ability to provide information on the mechanisms of immobilization.

APPROACH

A model can be thought of as a set of assumptions and the mathematical equations that can be deduced from those assumptions. The standard model used to interpret leaching test results is based on the following assumptions:

1) contaminant is being leached from an infinitely thick slab;
2) contaminants leach into an infinitely large bath of fluid;
3) all of the contaminant is mobile and the concentration of mobile contaminant is known and is constant throughout the slab at the start of the leaching test;
4) the contaminant is transported in one direction through the slab in accordance with Fick's law of diffusion applied with a constant diffusivity coefficient;
5) the contaminants do not react in any way.

Applying a material balance to the slab with these assumptions leads to the following partial differential equation, initial condition, and boundary conditions.

$$(1) \quad \frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2}$$

$C = C_{t0}$ for $t = 0$, all x

$C = 0$ for $t > 0$, and $x = +/- L$

where:
C = concentration of mobile contaminant, $[M/L^3]$
C_{t0} = concentration of mobile contaminant when leaching begins, $[M/L^3]$
D_e = effective diffusivity, $[L^2/T]$
t = time since leaching began, $[T]$
x = distance from center of slab, $[L]$
L = distance from center of slab to edge of slab (half-thickness), $[L]$

The above equations can be solved to give the concentration of mobile contaminant in the slab at any time. The internal concentration profiles are of little use by themselves. However, they can be integrated to obtain the amount of material that has left the slab at any time. This is normally expressed as the fraction of contaminant that has leached.

$$(2)\quad \frac{M_t}{M_o} = \left[\frac{4\,D_e}{\pi\,L^2}\right]^{0.5} t^{0.5}$$

where: M_t/M_o -fraction of contaminant leached, [ ]

This result can be used to determine the diffusivity of contaminant in the solidified waste. Measured values of Mt/Mo can be regressed against the square root of time and the slope obtained. The diffusivity can then be calculated directly from the slope. If the assumption of no chemical reactions is valid, the diffusivity calculated in this manner is the effective diffusivity. If the assumptions upon which the model based are not known to be valid, the diffusivity calculated with this procedure should be called an observed diffusivity. This approach uses the term "effective diffusivity" to refer to the coefficient that describes the physical transport of contaminant through the matrix. The term "observed diffusivity" refers to the coefficient that describes the effect of both physical transport and chemical reaction.

RESULTS

The suitability of the standard leach model could be limited if any of its major assumptions are not correct. The validity of the assumption of an infinitely thick slab can be evaluated by comparing estimates of Mt/Mo calculated with the standard model with those calculated using a model that assumes a finite slab thickness.[8] Figure 1 shows the error associated with assuming the slab is infinitely thick. Significant errors are not observed over the range of Mt/Mo that would typically be used. Therefore the assumption of an infinite slab does not limit the suitability of the standard model for most applications.

The accuracy of the assumption of an infinite bath can be evaluated with analytical solutions of models that describe how a finite slab leaches into a finite bath. The predictions made by these models depend on the relationship between the concentration in the slab and the concentration in the bath that would exist if the leaching were allowed to continue forever. This relationship is affected by the ratio of the volume of the slab to the volume of the bath, and by any correction factor needed to express slab concentrations on the same basis as bath concentrations. A typical correction factor would be applied when slab concentrations are expressed on the basis of the total slab volume and only a fraction of the volume of the slab actually contains water. In this case, the correction factor would be the porosity of the slab. The combined effect of these factors is expressed in a term represented by α.

$$(3)\quad \alpha = \frac{V_b}{V_s\,K}$$

where: α - coefficient, [ ]
V_b - volume of bath, [L^3]

V_s = volume of slab, $[L^3]$

K = ratio of contaminant concentration in slab to equivalent concentration in bath, [ ]

Figure 2 shows the extent to which the assumption of an infinite bath leads to errors in the standard model. When α is large (relatively large bath volume, or small correction factor), the error is manageable. When α is small, the error is larger but it is predictable. The error is nearly proportional to the fraction leached. The error in the ultimate fraction leached that is incurred by the standard model can be calculated by knowing that the standard model predicts $(Mt/Mo)inf = 1.0$ and the finite bath model predicts $(Mt/Mo)inf = \alpha/(1 + \alpha)$. The error in the standard model can then be estimated at each value of Mt/Mo by assuming it is linearly related to Mt/Mo. This result can be used to design leaching experiments that do not lead to significant errors when the standard model is applied to interpret results.

(4) Relative Error in M_t/M_o (%) = $(M_t/M_o)_{meas}\ (100\%/\alpha)$

where: $(M_t/M_o)_{meas}$ = fraction of contaminant leached as measured using the standard model, [ ]

The most significant error associated with the assumption of a constant, known initial contaminant concentration would likely occur when a fraction of the contaminant is completely immobilized by some physical or chemical process. If this were not recognized, there would be an error in calculating the fraction leached, because the wrong value for the initial contaminant mass (M_o) would be used. Observed diffusivity calculated using the conventional model would be in error in proportion to the fraction of contaminant that is mobile (F_m).

(5) $(M_t/M_o)_{meas} = F_m\ (M_t/M_o)$
$= F_m\ (4\ D_e/\ L^2)^{0.5}\ t^{0.5}$

(6) $D_{obs} = (F_m)^2\ D_e$

where: D_{obs} = observed diffusivity, i.e. that value calculated using standard model, $[L^2/T]$

F_m = fraction of contaminant that is mobile, [ ]

The assumptions that the contaminants are completely mobile and that they do not react chemically are probably the most likely to be invalid. The effect of chemical reactions on observed diffusivities can be evaluated using modifications of the standard model. Precipitation and sorption are two of the most likely chemical reactions to affect contaminants in solidified wastes.

If precipitation occurs, a portion of the contaminant will be converted to the immobile solid form. As mobile contaminant leaves the slab, the precipitate will tend to dissolve to maintain the mobile phase concentration at the saturation concentration for that precipitate. This process can be modeled rather simply by assuming that the dissolution reaction is rapid compared to the diffusion step, and that a pseudo-steady state concentration profile is set up in the slab.[9] This model can be solved to provide the following estimate for Mt/Mo as a function of time.

$$(7)\quad \frac{M_t}{M_o} = \left[\frac{2\,D\,(K_p + 0.5)}{L^2 (K_p + 1)}\right]^{0.5} t^{0.5}$$

$$(8)\quad D_{obs} = \frac{\pi\,(K_p + 0.5)\,D_e}{2\,(K_p + 1)^2}$$

$$\text{if } K_p \gg 1, \text{ then } D_{obs} = \frac{\pi\,D_e}{2\,(K_p + 1)}$$

where: K_p = ratio of mass of contaminant in immobile precipitated phase to mass of contaminant in mobile soluble phase when leaching begins, [ ]

Since $(K_p + 1) = 1/F_m$, then when $K_p \gg 1$:

$$(9)\quad D_{obs} = \frac{\pi\,F_m\,D_e}{2}$$

The precipitation model predicts the same dependence of Mt/Mo on time as does the standard model. However, the observed diffusivity that would be calculated using the standard model is smaller than the effective diffusivity. The difference is due to the effect of chemical immobilization of the contaminant through precipitation. The model presented above is able to separate the chemical and physical factors that effect leaching behavior.

Another chemical process that could effect leaching behavior is sorption/desorption. In this process, the contaminant is exchanged between an mobile form in solution and an immobile form on the solid matrix. The relation between immobile and mobile forms can be expressed in terms of an isotherm. By assuming that the exchange between mobile and immobile forms is rapid compared to the process of diffusive transport, the partial differential equation describing leaching can be converted to the following.

$$(10)\quad \frac{\partial C}{\partial t} = \frac{D_e}{1 + (dC_i/dC)}\;\frac{\partial^2 C}{\partial x^2}$$

where: (dC_i/dC) = derivative of isotherm relating the concentration of immobile contaminant (C_i) to the concentration of mobile contaminant (C), [ ]

If sorption is linear, the derivative in Equation 10 will be a constant, and will equal K_p. Therefore, the observed diffusivity can be related to the effective diffusivity by the following.

$$(11)\quad D_{obs} = \frac{D_e}{1 + K_p} = F_m\,D_e$$

This demonstrates how the observed diffusivity can be shown to be affected by physical factors (D_e) and chemical factors (dC_i/dC). When linear sorption occurs, the observed diffusivity is proportional to the effective diffusivity. However, when nonlinear sorption occurs, the observed diffusivity is a function of the concentration of mobile contaminant. The Langmuir isotherm is an example of a nonlinear isotherm that often used to describe the equilibrium relationship between sorbed and soluble components.

$$(12)\quad C_i = \frac{C_{i,max}\; b\, C}{1 + b\, C}$$

$$(13)\quad \frac{d\, C_i}{d\, C} = \frac{C_{i,max}\; b}{(\, 1 + b\, C\,)^2}$$

When nonlinear sorption occurs, Equation 10 must be solved numerically to determine how contaminants leach from the solid. An orthogonal collocation technique[9] has been developed to do this. Initial results indicate that the model with sorption/desorption predicts that the fraction leached will be proportional to the square root of time, which is similar to the results obtained for the model without reaction. However, the slope of the plot is substantially less than would be obtained if sorption did not occur. It may be possible to make "first-approximation estimates of observed diffusivity by assuming that the concentration of mobile component is low. With this assumption, the denominator in Equation 13 approaches one, and the observed diffusivity is proportional to the effective diffusivity. When applied to preliminary data, this approach predicted the effective diffusivity within a factor of two.

The results presented above for leach models incorporating chemical reactions shows how these processes can strongly affect the value of the observed diffusivity measured in standard leaching tests. Large variations in observed diffusivities would be expected for contaminants that display different chemical behavior. Reported values of observed diffusivities support this observation. One study reported observed diffusivities to range from 5×10^{-9} cm^2/s for sodium to 4×10^{-16} cm^2/s for lead.[5] Sodium would be expected to be relatively nonreactive, while lead would be likely to precipitate or sorb in wastes solidified with portland cement. The effective diffusivities for sodium and lead should vary by less than a factor of two,[10,11] so the importance of chemical reactions is clear in this case.

Based on the analysis of the standard leach model and alternative models the following conclusions can be drawn.

1. Errors in calculating the observed diffusivity that are associated with assuming an infinitely thick slab and an infinite bath volume can be kept at small levels by proper design of leach tests.
2. Errors in calculating the observed diffusivity that are associated with complete and permanent immobilization of a fraction of the contaminant are directly related to the fraction immobilized. This fraction is difficult to measure unless very long leaching tests can be conducted.
3. Observed diffusivities depend on physical and chemical factors. The effect of the chemical factors of precipitation and sorption can be quantified. In both cases, the models incorporating chemical processes predict behavior in agreement with the form of the standard model, but with observed diffusivities lower than effective diffusivities.
4. Simple models for leaching with linear sorption or with dissolution of a precipitate show that the observed diffusivity

should be approximately equal to the effective diffusivity times the fraction of contaminant that is mobile. A simple model for leaching when a fraction of the contaminant is completely immobilized predicts that the observed diffusivity is equal to the effective diffusivity times the fraction that is mobile squared.

5. Leaching results should be reported as observed diffusivities, unless it is known that chemical factors are not affecting leaching rates.

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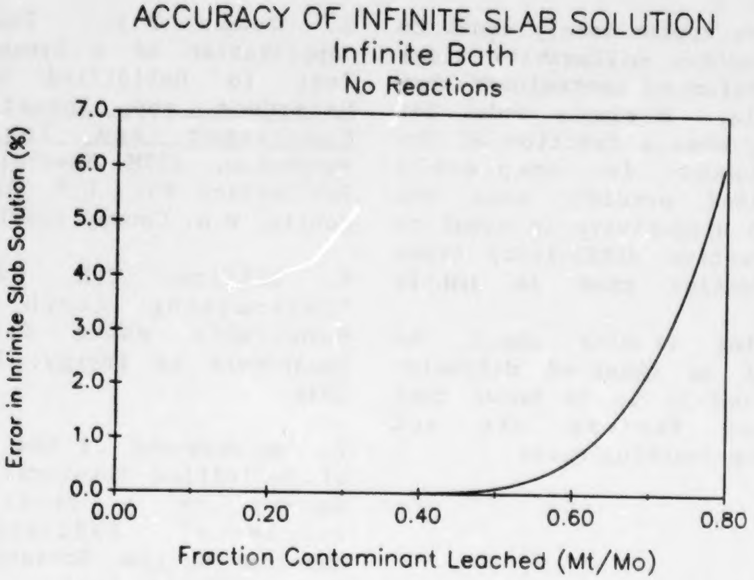

Figure 1. Accuracy of Infinite Slab Solution

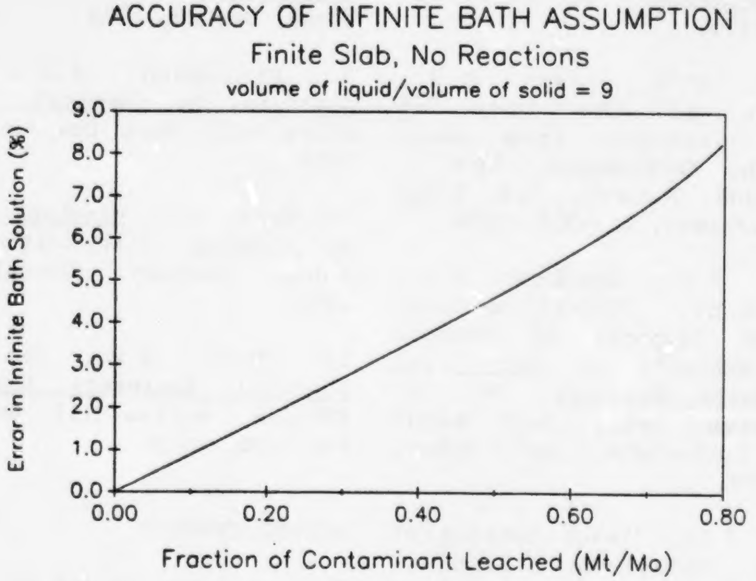

Figure 2. Accuracy of Infinite Bath Solution (α = 9)

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SOLIDIFICATION OF FILTER ASHES FROM SOLID WASTE INCINERATORS

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ABSTRACT

Residues from flue gas purification of Swiss MSW incinerators consist primarily of silicates, alkaline and alkaline earth metals, aluminum compounds, carbonates, chlorides and sulphates. Since trace metals such as Zn, Cd or Hg may be leached from these residues, treatment of the ash is required in order to prevent hazardous emissions from ash landfills. The stabilization of electrostatic precipitator ash, dry scrubber ash and wet scrubber sludge with various cement based binders improved the structural quality as well as the leaching behaviour. The results for leaching and stability from field tests compared favourably with laboratory experiments. For a stabilization which retains the hazardous constituents in the landfill body for long periods of time, it proved to be necessary to equilibrate the ashes with water prior to treatment with a binder. By appropriate stabilization of the pretreated ashes, a compressive strength > 1 N/mm^2, mass losses after twelve wet/dry and freeze/thaw cycles of $< 10\%$, and metal leaching < 1 ‰ of total metal present were obtained.

INTRODUCTION

For modern urban areas, the importance of the incineration of municipal solid wastes (MSW) increases due to the scarce space for landfilling. By the combustion process, the mass of residues which has to be disposed of in landfills can be reduced by about 80 %. Still, after incineration one fifth of the MSW remains to be landfilled in the form of bottom ash, filter ash or scrubber sludges. MSW contains considerable amounts of the national consumption of many materials. For highly urbanized regions, it has been estimated that as much as 20 % of the imported cadmium and lead is contained in the MSW. During incineration, many elements are concentrated in the offgas and removed by the air pollution control devices. Therefore, the filter ashes or scrubber sludges act as very important carriers for certain elements (Hg, Cd, Pb, Sn, Sb etc.) from the antroposphere to the environment, or where economically possible back into consumption cycles. It is of chief importance to control the quality and the treatment including the final storage of the residues of MSW incineration. This is further emphasized by the fact that due to the high content in chlorides, the filter ashes contain a large fraction of mobile heavy metal compounds.

The present paper focuses on the chemical and physical immobilization of hazardous compounds in filter residues from MSW incinerators. It is a summary based on solidification and leaching experiments which have been performed by various Swiss institutions from 1984 to 1987.

PURPOSE

The objectives for the treatment of residues from MSW incineration in Switzerland are: 1. the transformation of leachable hazardous constituents into compounds which are not mobile under landfilling conditions for long periods of time (<10^3 years), and 2. if economically feasible, the recycling of metals by further concentration and use as a raw material in smelters. In this paper, we discuss the stabilization of residues from flue gas cleaning with *cementious binders*. The objectives for this treatment are:
1. Minimize the leaching rate by minimizing permeability and diffusivity, 2. minimize the leachate concentration of metals by producing metal species of low solubility, and 3. prevent long term acid corrosion by establishing a high buffering capacity at the proper pH level.

The goal of this paper is to present composition and behaviour of a number of filter ashes and to discuss various ash treatments which may potentially reach the desired goal of long term immobilization. The following questions are addressed:

1. What is the composition of the filter residues of various wet and dry cleaning systems of MSW incinerators?
2. What is the leaching behaviour of these products?
3. How is the leaching behaviour and the stability of the filter ashes improved by the addition of simple stabilizers such as cement?
4. What general conclusions can be drawn for the immobilization and solidification of filter ashes?

APPROACH

The composition of filter ashes from five Swiss municipal solid waste incinerators, equipped with either electrostatic precipitators (ESP), spray dryer absorbers, or wet scrubbers, has been determined by the usual analytical methods. The leaching behaviour of the untreated filter ash has been examined by laboratory leaching experiments. Samples of filter residues have been solidified with various methods. The treated samples were tested by physical and chemical methods in the laboratory. Three mixtures of cement based binders and ashes have been tested for leaching in field experiments of various sizes.

element [g/kg]	A	B	C
SiO_2	270	150	n.d.
Al	80	50	4
Ca	60	230	260
Na	50	6	4
K	40	12	3
Mg	18	8	7
Fe	35	8	33
Cl	60	120	5
S	30	40	80
C	30	27	50
P	6	3	0.4
Zn	25	12	8
Pb	9	4	3
Cu	3	0.8	0.3
Sn	4	n.d.	2
Cr	1	0.2	n.d.
Ni	0.2	0.1	n.d.
Cd	0.4	0.2	0.1
Hg	0.1	0.3	1

Table 1: Mean values of some constituents of residues from three flue gas cleaning systems. Due to the high content in CaO, the pH value of a mixture of water and ash A increases after three days of mixing from 7 to 11.6. The pH value of the mixture of ash B with water increases to about 12. (A: esp ash, B: dry scrubber (spray absorber) ash, C: wet scrubber sludge)

Composition and Behaviour of Filter Ash, Dry Scrubber Ash and Wet Scrubber Sludge

Filter ash from MSW incinerators consists primarily of silicate, aluminum, and alkaline and alkaline earth metals (cf. table 1). The prevalent metal species are mainly silicates, oxides, chlorides and sulphates, with carbonates and phosphates as minor compounds. In the products from dry scrubbing, the calcium and chloride concentrations are enhanced due to the addition of $Ca(OH)_2$ and the removal of HCl from the offgas. Most other elements are less concentrated in the dry scrub-ber product because of the dilution effect of the calcium chloride. An exception is mercury, which appears to be sorbed by the surface of the dry scrubbing agent and hence is partly removed from the offgas.

The difference between the esp dust and the wet scrubber sludge concerns mainly chloride, phosphorus, aluminum, and other mobile elements, which are in part removed in the aqueous phase. If not removed separately by ion exchange or precipitation, mercury is enriched in the scrubber sludge. More important is the fact that scrubber sludges are generated in water, which means that they have gone through such processes as dissolution, hydrolysis, neutralization and precipitation, and that they are more or less in an equilibrium state with water. This is not the case for dry products, which upon contact with water will go through many processes. It is therefore more difficult to stabilize dry products; in most cases it is advisable to thoroughly wet or even wash the dry products before solidification.

In contact with water, alkaline and other metal oxides are hydrolysed, resulting in a significant increase of the pH value of the aqueous solution from 6-7 to 9-10. The metal chlorides present in the ash are readily dissolved when leached with water. They will precipitate as hydroxides when the pH value increases due to the contact with water. Thus, an important fraction of heavy metals such as cadmium and lead are leached from the ash at the first contact with water. With longer residence times in water, they will be retained in the ash/water mixture because the pH value increases to around 10-11. In the laboratory leaching experiments, which lasted 14 days, no significant differences in the metal leaching behaviour of pulverized small grain ash samples versus solidified (no binders) samples were detectable.

The content of organic substances in the filter ash ranges from 10-50 g/kg (Brunner et al,1987). Although the content of certain micropollutants such as PCDD and PCDF, PAH, chlorinated benzenes and phenols in the mg/kg range is well known, there exists no detailed information on the nature of the bulk of the organic carbon in the ash. A large fraction is easily extractable with organic solvents. Of all the organic substances investigated, the chlorinated phenols are the most likely to be leached from a filter ash landfill.

Solidification Experiments

The objective of the experimental work was to find simple recipes to solidify and immobilize products from flue gas cleaning by the addition of commercially available binders, and to test some of the promising recipes in the field. In many laboratory experiments, proctor cylinders (d=56 mm, h=100 mm) of various mixtures were produced (table 2). The cylinders were tested for stability and for leaching of selected metals and nonmetals. The data of the leaching experiments have been used to

ash type	Composition of mixture %ash	%cement	%water
A	40	40 HTA	20
B1	60	20 HTA	20
B2	30	30 HTS	40
C	45	15 HTA	40

Table 3: Solidification recipes for ashes, resulting in minimum mass losses after 12 wet/dry and freeze/thaw cycles and a compressive strength of > 1 N/mm^2. A: esp ash, B1: dry scrubber ash, B2: dry scrubber ash washed, C: wet scrubber sludge; HTA High aluminum cement plus retarder; HTS calcium silicate cement (24 % Si).

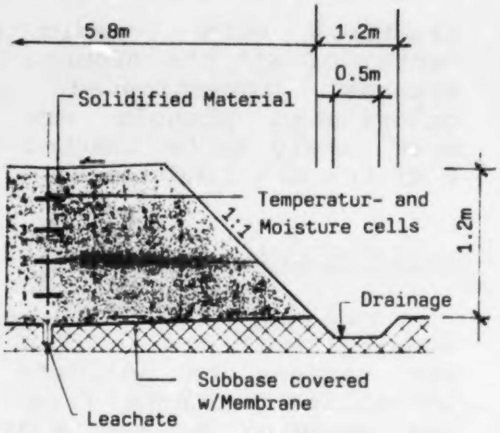
5.8m
1.2m
0.5m
Solidified Material
Temperatur- and
Moisture cells
1.2m
Drainage
Subbase covered
w/Membrane
Leachate

Fig.1a Test Site A. Covered w/roof. Dry scrubber ash + slag + binder (HTA)

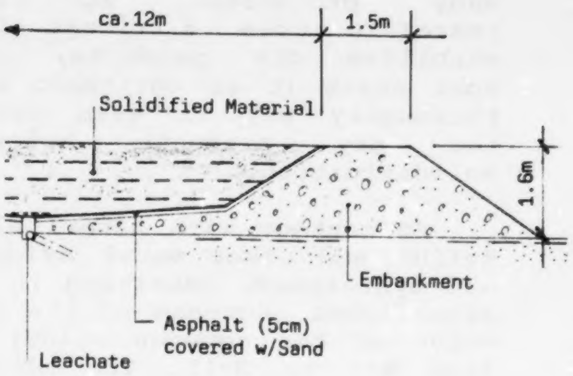
ca.12m
1.5m
Solidified Material
1.6m
Embankment
Asphalt (5cm)
covered w/Sand
Leachate

Fig.1b Test Site B1 and B2.
B1: Dry scrubber ash + sand + HTA
B2: Dry scrubber ash + slag + HTA + Trisilicate

calculate a "pseudo" diffusion coefficient according to the US EPA Uniform Leaching Procedure.

Table 3 summarizes the recipes and the products which have been succesfully solidified. Prior to testing, the samples were cured for 10 days at 20 °C and 98 % rel. humidity. The physical testing included the compressive strength, the resistance to freez/thaw cycles as well as dry/wet cycles. A compressive strength of > 1 N/mm^2 and a loss of mass < 10 % after 12 freeze/thaw and wet/dry cycles, respectively, was considered as appropriate for disposal in a final storage site.

The cyclic freeze/thaw testing is considered to reflect expansion forces while the wet/dry tests simulate shrinking forces on the treated material.

The chemical analysis comprised the measurement of the concentrations of Cl, Pb, Cu, Zn, Cd, in a leachate which was obtained after consecutive leaching with deionized water in equilibrium with air, and in certain cases in equilibrium with CO_2.

In the field experiments, the mixing, handling, the solidification and the leaching behaviour of the various filter products was tested. The laboratory test methods were compared to the field results in order to check their validity. Three experimental landfills of 30 to 150 m^3 volume were constructed, each containing dry scrubber ash solidified by different methods. One of these test sites was covered by a roof and run under strictly controlled and enhanced raining conditions (cf. fig. 1a and 1b).

PROBLEMS ENCOUNTERED

Time proportional sampling of leachates proved to be insufficient to follow the leaching behaviour in the field. In order to collect leachates from individual rain events, sampling was done manually in relation to the rain events. Also, it was impossible to obtain a leachate which actually had penetrated the landfill body. The collected leachate was rainwater which ran along the surface and the interface to the base liner of the solidified body. This reminds one of the fact that most laboratory tests are performed with a mass-to-leachate ratio which is very convenient for laboratory testing (1:3 to 1:20) but does not reflect the actual field conditions where the mass to leachate ratio is usually much higher (5:1).

The rapid setting, typical for HTA cements, had to be counteracted with retarders. Due to the over-stochiometric addition of $Ca(OH)_2$ and the alkalinity of the binder, the leachate of the *dry scrubber material* was highly alkaline ($pH<12$). Thus the leaching of Pb as a soluble hydroxo complex is a problem. The addition of trisilicates (Na_2S) up to 1% of the binder was only partly effective.

After several months of exposure to rain and atmosphere, effects of weathering were discerned at the surface of the landfill body. They included disintegration of the surface into grains (site B1) and/or squaling due to ettringite formation (site B2). These crystallization effects can be diminished with a simple pretreatment of the ash with water. The handling of the material proved to be difficult. For rapidly reacting binders, it is not advisable to use continuously operating mixing devices. When batching with a regular concrete mixer, the cleaning and maintenance of the equipment became a serious problem. If possible the water used for cleaning should be recycled. The evaporation from the landfill was enormous (1 mm/h) for certain weather conditions .

Highly mobile salts such as NaCl and $CaCl_2$ were readily leached from the landfill body. The high concentration of chloride (up to 40 g Cl^-/l) may have a negative impact on the aquatic ecosystem of a small receiving water. No binding connection developed between the individually compacted layers of the landfill.

RESULTS

The following results were obtained: It is possible to stabilize a pretreated (e.g. washed) filter ash with cement binders so that it becomes structurally stable for several decades. For a successful immobilization and solidification, it is necessary to equilibrize filter ash with water prior to mixing it with binders. The leaching of metals and nonmetals from the filter ash can be much reduced by the stabilization process. Nevertheless, for a few metals such as lead and zinc complete retention in the landfill body

residues	ESP ash, dry and washed	dry scrubber ash, dry and washed	wet scrubber sludge
binders	PC, PCHS, HTS, HOZ, Bitumen	HTA, HTS, PC	PC, HTA, HTS
aggregates	slag, klinker, calcium	slag, sand	-
additives	-	retarders, Na_2S	-

Table 2: Summary of ashes, binders, aggregates and additives tested; PC: portland cement, PCHS: PC with high resistivity for sulfate, HOZ: blast furnace slag, HTA: high aluminum cement, HTS: high silica cement.

residue type		mixture		results of leaching test						
	ash	bind.	H_2O	Cd		Zn		Pb		Cl
				A	B	A	B	A	B	A
	%	%	%	%	-	%	-	%	-	%
untreated esp ash	100	-	-	12	10	2	11	4	10	52
solidified esp ash	40	40$^{2)}$	20	0.01	15	0	15	0.01	15	28
solidified mixture dry scrubber ash and 25% bottom ash	35	18$^{2)}$	22	<0.01	15	0.04	14	0.5	9	nd
washed and solidified dry scrubber ash$^{1)}$	32	28$^{3)}$	40	0.4	11	0.4	10	0.02	13	1
untreated wet scrubber sludge$^{4)}$	100	-	-	6	10	8	9	3	10	nd
solidified wet scrubber sludge$^{4)}$	50	10$^{2)}$	40	1	13	0.5	15	0.03	15	100

Table 4: Leaching tests according to US EPA uniform leaching procedure; A: % metal cumulatively leached during 11 leaching cycles; B: - log D_e; D_e = Diffusion coefficient after 11 leaching cycles; $^{1)}$ leaching with CO_2 saturated water; $^{2)}$ HTA; $^{3)}$ HTS; $^{4)}$ neutralization with $Ca(OH)_2$. Range of leachate concentrations (mg/l): Cd 0.0002-4, Zn 0.02-700, Pb 0.001-6

was not achieved by the technics employed in this work. The results obtained in the field compared favorable to the laboratory experiments.

Structural Stability

Some of the mixtures studied appear to produce stabilization effects with satisfactory physical properties (compressive strength >1 N/mm^2 and resistant to 12 wet/dry and freeze/thaw cycles). It has to be emphasized, that the laboratory tests applied allow to qualify the stabilized material for short to medium terms only. Thus, it is not possible to judge the structural stability for periods longer than about one hundred years. Based on the field experiences, it became obvious that the solidification of dry filter ashes from esp, and much more pronounced from dry scrubbing processes, contain large amounts of highly active materials such as CaO, metal chlorides and others. The CaO will react with water and will subsequently produce a leachate with a high pH value between 10.5 to 12.5. These reactions are not completed during the short stabilization process of the ash products. In the landfill, these reactions will continue, and are often accompanied with a change in volume and physical stability. In order to overcome these adverse effects, it proved to be necessary to wash the filter ashes first. The products of such an enhanced and controlled water contact are much better suited for long term stabilization. This fact might have implications on the type of flue gas cleaning technology to be chosen.

Chemical Immobilization

Table 4 shows the leaching results of some typical treated and untreated ash test specimens. From *untreated residues* of esp as well as dry and wet scrubbers large amounts of heavy metals and chlorides are leached when landfilled [Brunner and Baccini, 1985, Sawell et al, 1988]. The initial washout behaviour is controlled by fast reactions, while the longterm stability in the landfill may be determined even by very slow reactions like exchange of constituents of the cement matrix or crystallization.

The chemistry of the slow reactions of the *stabilized ashes* has not been determined yet. The short term leaching is mainly pH controlled and consists of an initial wash off of the highly soluble metal chlorides. This may result in a significant (> 1%) loss of e.g. cadmium and lead. The initial loss can be prevented if the ash is put into contact with water until the soluble metals are precipitated as hydroxides due to the hydrolysis reaction of the CaO with water. If alkaline binders such as portland cement are added to improve the structural stability of the ash, *the pH value should be kept below 12* in order to prevent the mobilization of lead, zinc and other metals due to the formation of soluble hydroxo complexes.

A sufficient mixing time (e.g. > 3 min. per m^3 total mixture) is required for optimum immobilization effects.

Comparison of Laboratory Tests to Field Tests

In order to assess the behaviour of the tested materials, it is indispensable to know the composition of the ash mixtures. Laboratory tests should be directed towards the understanding of the chemical, physical and structural reactions which take place during the interaction of the ash, the binders and the environment (water, air, biosphere). Standard tests which yield certain factors like a "pseudo" diffusion coefficient or the cumulative leaching of an element from a test sample, may be used additionally to compare various stabilizing recipes; they are generally not suited to predict the *longterm behaviour* of reactive ash materials in landfills. The following statements have been derived from the laboratory testing and were confirmed by the field tests:

Tests with deionized water are well suited to investigate the short term behaviour of the ashes. The results compare well with the field experience of the first few months of exposure to the weathering. The long term behaviour is better (but by no means completely) understood if acidic leachates such as carbonic acid are used as leaching agents, e.g. to titrate the buffering capacity.

Laboratory and field tests show: Chloride is highly mobile in the treated and untreated filter ash and can hardly be retained in the landfill body. An exception may be the formation of Friedel salts with HTA ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$).

Lead and zinc are leached from the *treated and untreated* ash samples if the pH value is allowed to surpass 12 (cf. also Sawell et al, 1988). There is a decrease in the concentration of leached metals with increasing leaching (-time and -volume) in laboratory tests as well as the field experience.

Results from laboratory tests of solid proctor cylinders are generally similar to the results of tests of the *pulverized* proctor cylinder; this is explained by the hypothesis that the chemical immobilization of metals is more important than the physical exclusion of water. However, in the field the solidification decreases the penetration of water into the landfill body very much, so that due to the reduced water flow the material transport is highly decreased also, at least in the first few months. The future development of the water flux through the body has not been assessed yet.

The laboratory testing of the structural properties did not allow to predict the field observations of the deterioration of the structure of the landfill body. The water transport in the field is much different from the laboratory tests. The difficulties of handling the ash and how to solve them are only experienced in the field.

Outlook

Swiss guidelines for waste management require long term safety for all products of waste treatment. In the case of landfills ("final storage sites" [Baccini, 1989]), this objective has to be reached by treating wastes before landfilling, so that no aftertreatment of the effluents of the landfill is needed even for long time periods. Residues from FGC systems show a relatively narrow composition range. They are considered a hazardous waste, which preferably should be disposed of separately (treatment and mono-landfill). Thus, a future reuse as an ore might be possible. The stabilization improves the quality of the filter ashes considerably, so that most constituents are retained in the landfill body. Nevertheless, the longterm fate of some elements is not well known yet. It is therefore still an open question, if other kinds of processes such as high temperature treatment of the filter ash come closer to the high goal of the Swiss guidelines.

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EVALUATION OF STABILIZATION-SOLIDIFICATION TECHNIQUES

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ABSTRACT

Among the techniques applied to treat polluting residues in France for the past ten years has been the mixing of pollutants with reactive agents in order to "fix" the contaminants and to give them a solid consistancy The first applications of these stabilization/solidification processes occured in 1978 in the treatment of oil residues from the AMOCO CADIZ spill. They have also been used for the treatment of a mayor dump site for petroleum residues, for the disposal of mineral sludges of a detoxication plant, and for the rehabilitation of sites contaminated by various industrial residues, specially acid tars generated by oil refining plants.

Although from the beginning these techniques appeared to be able to transform filthy lagoons into solid and apparently safe areas, it was necessary to evaluate their efficiency and to determine the conditions and limits of application.

In the beginning of the eighties, laboratory studies were performed to answer these questions and more recent tests of the present state of sites treated up to ten years ago have been carried out. Laboratory evaluation showed that processes using lime as the main reactive agent are efficient in treating organic waste (specialy acid tars) and that those using pouzzolanic materials are better for fixing mineral contaminants. However, tests of treated sites show that although these sites have a satisfactory appearance without any harmfull effect observable in their environment the performances of the treated material are not always as well "fixed" as desired This situation may be partly explained by the unability of some treatment processes to fix some specific contaminants, but it also indicates the lack of an effective analytical technique and of a clear set of performance requirements at the time of treatment . Since that time, these points have been improved. However, this emphasize the necessity for the specification of evaluation tests, especially for the estimation of long term releases of contaminants from treated material. This has become more important as stabilization solidification techniques seem to have a wide opportunity of developpement for the treatment before disposal of waste which are the residues of other treatment (i.e incineration) or which cannot be treated by other means.

INTRODUCTION

In France, two main commercial stabilization-solidification processes have been applied : the EIF-Ecologie process based on the use of lime as main reactive agent an the TREDI-PETRIFIX process based on the use of pouzzolanic material.

In the EIF-Ecologie process, the waste is excaved and placed in a shallow layer above the ground at the disposal site and the reactive agent is spread on the waste and mixed with it. The treated material is then disposed and compacted in shallow layers.

In the Petrifix process the waste is extracted, usually by pumping and transported to a modular system of mixing and fed with the adjusted quantity of reactive agent, the treated material is then disposed at the site.

PURPOSE

Evaluation of stabilization/solidification processes is needed for the physical caracteristics of the treated materials as well as for the capacity to fix the various contaminants. For the case of the two processes presented, laboratory evaluation was carried out in 1980 and 1982 and field efficiency has been recently evaluated at the occasion of a study realized within the NATO CCMS Pilot Study Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater.

APPROACH

A - Laboratory studies

1 - Evaluation of EIF-Ecologie process

The study was carried out for the application of this treatment to petroleum sludges and to acid tars. It consisted in a leaching test with agitation of a shallow cylinder of compacted treated waste during 48 hours in demineralized water (100 g per liter). The result of the analysis of leachates are gathered in the following table 1 (figures given in mg/kg except pH and resistivity).

TABLE 1 : EIF ECOLOGIE Process (Units in mg/kg except for pH and resistivity)

	Acid tar		Petroleum sludge1	
	untreated	treated	untreated	treated
pH	1.15	12.15	7.12	12.10
resistivity /cm	37	157	2960	161
COD	372840	3718	220	4080
Hexane extract.	9800	75	720	200
Chloroforme extract.	39400	396	4040	63.5
Ag	0.5	0.13	< 0.2	<0.1
Cd	1.4	0.25	<0.2	0.2
Cu	7.6	0.2	0.4	0.1
Cr	6.8	0.21	<0.2	<0.1
Fe	165	0.40	6.5	0.2
Mn	3.0	0.14	1.0	<0.1
Ni	6.0	1.33	1.0	1.0
Pb	37.0	3.9	6.0	1.2
Zn	450	0.62	4.7	0.4
Ca	800	6350	170	4235

Then, similar tests were performed to compare pure water to other solvents : solution representing athmospheric water (acid rain), water polluted by residues of aerobic degradation of organic material and water polluted by residues of anaerobic degradation of organic material. No significant differences were found in the release of contaminants, except for the last extractive solution in which the contaminants released were about two times those released in other solutions.

2 - Comparative evaluation of stabilization-solidification process

An other study was realized in 1982 that compared the efficiency of different treatment methods to stabilizeand solidifie sludges. The selected residues were representative of inorganic sludge neutralized by sodium hydroxide (sludge A), inorganic sludge neutralized by lime (sludge B), petroleum sludge (sludge C). The following table 2 represents the characteristics of the liquid phase of the untreated sludge (figures in mg/l except pH and resitvitivy (Ω cm)

TABLE 2

	Sludge A	Sludge B	Sludge C
pH	9.36	9.42	12.07
resistivity	14	14	111
COD	-	-	6291
chloroform	-	-	2112
phénol	-	-	90
Sulfate	30006	3527	-
Chloride	62166	70034	601
Nitrate	5900	6052	52
Sodium	65780	7480	496
Caldium	377	54400	75
Potassium	105	154	2541
Cd	0.9	2.5	<0.12
Cr tot.	2990	1683	0.8
Cr6+	2760	1598	<0.24
Cu	0.9	1.5	0.5
Fe	2.3	3.4	4.1
Mn	<0.2	0.85	<0.2
Ni	1.4	5.5	<0.6
Pb	2.0	8.1	12.3
Zn	1.8	4.3	1.4
Li	31	140	0.9

Test of physical characteristics and various leaching tests were applied to treated materials : leaching with different solvants : pure water, acid rain, water contaminated by municipal waste. There after are presented some of the mains results of these investigations applied to the EIF-Ecologie and TREDI Petrifix processes.

Characteristics of treatment

TABLE 3

		Sludge A	Sludge B	Sludge C
TREDI Petrifix	Sludge (kg)	33.3	33.3	46.55
	reagent (kg)	26.7	26.7	77.20
EIF Ecologie	Sludge (kg)	38	35	53.1
	reagent	10.45	14.40	27.60

Mechanical propecties of treated materiel

(Bending strength (daN/cm2) and compressive strength (daN/cm2) 28 and 90 days after treatment)

TABLE 4

		Sludg A		Sludge B		Sludge C	
TREDI Petrifix	days	28	90	28	90	28	90
	B.Str.	31.5	-	23.5	61	19	12
	C.Str	121	170	105	320	120	210
EIF Ecologie	B.Str.	5	3				
	C.Str.	7.7	12	3.12	19	-	-

Freeze-Thaw durability (10 cycles)

Sludge treated by EIF-Ecologie : no alteration observed. Sludge treated by TREDI Petrifix : fissuration of treated inorganic sludge during the third cycle.

Wet - dry durability (10 cycles)

Sludge treated by EIF-Ecologie : no alteration observed - liquid phase colored in yellow in the case of inorganic sludge (Cr)

Sludge treated by TREDI Petrifix : alteration during the third cycle (mineral sludges) no alteration for petroleum sludge.

B - Fiel study

Within the scope of the NACO CCMS Pilot Study Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater, the evaluation of the present state of sites treated by EIF-Ecology and TREDI Petrifix has been carried out. For every treatment technique, two treated sites have been evaluated. Their main characteristics are summarized in the following table 5.

Sampling

For every site, three sampling trenches were realized and for every trench three samples of three kilograms of material were taken : one of the treated material from the upper layer of the treated section ; one of the treated material from the middle layer, and one from the ground material located under the treated zone. The idea was that the upper sample might be considered as representative of the treated material in contact with biosphere conditions : freezing, leaching by infiltrated water, the middle sample representative of the average treated material and lower sample would give an estimation of possible releases of contaminants from the treated materiel. However, it appeared that the representativity of the upper and lower sample was not reliable and finaly we considered only the middle sample as representative.

Tests

- measuring of physical properties

. water content
. permeability
. compressive strength

- leaching tests

In France, at the present time, there are no specific standardized tests for evaluation of contaminated material treated by stabilization-solidification. However, investigations are now carried out that will propose such tests within less than one year. Consequently, it was decided :

a) to perform for every average sample the present leaching test (called INSA test) applicable to waste material candidate for landfilling in special industriel waste landfills. The main features of this test are :

- extraction solvent : demineralized water saturated with CO2 and air (pH about 5),
- tested material crushed in parts smaller tham 4 mm,
- 100 g of material mixed with 1 liter of extraction solvent,
- extraction of solution for analysis after 16 hours of agitation.

Two successive extractions (1 and 2) have been carried out (table 7)

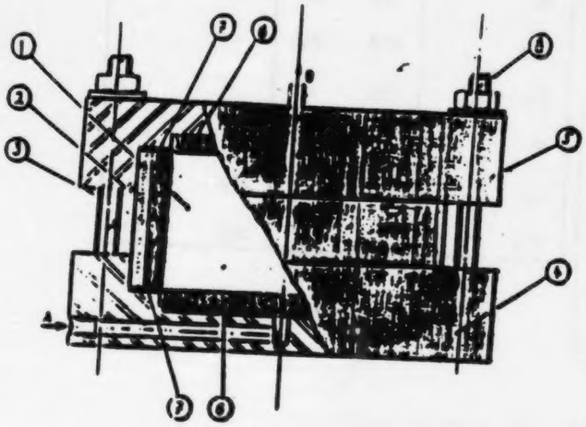
TABLE 5

Site	Waste	Quantity	Contam.	Year of treat	Technique
A	Petroleum waste	24 000 t	HC,metals	1978	EIF-ECOLOGIE
B	Acid tars	25 000 t	HC,acids, metals	1984	EIF-ECOLOGIE
C	Agro-industrial wastes	7 500 t	organics	1980	TREDI-PETRIFIX
D	Tanning sludges	9 000 t	cronium ammonia	1982	TREDI-PETRIFIX

b) In addition, in order to take in account the specific characteristics of solidification techniques it was decides to perform the new test which is now prepared to be later standardized for evaluation of solidified material.

This test called oedometric pressure leaching test is based on the use of a pressure permeater, a section of which is represented on the following figure 1.

FIGURE 1



1 - Sample
2 - Cylinder of confinement
3 - COntact resin
4 - Lower baseplate
5 - Upper baseplate
6 - Porous stone
7 - Filler joint
8 - Stud bolts

The test is performed first to give an evaluation of the permeability of the treated material, then the oedometer is operated for leaching test. The pressure is adjusted in order to get a discharge of 0.01 cm3/s (36 cm3/hour). Successive extractions are carried out and it is possible to add separatley the extracted quantities of every contaminant and to represent their variation in function of the quantity of the liquid discharged through the sample;

This function is hyperbolic and its interpretation allows the evaluation of the total quantity of the considered contaminant which can be extracted if the volume of extraction liquid or the time of extraction was infinite. The resulting figure will be considered as the maximum extractible quantity of the considered contaminant (mg/kg). For the present study, five successive extractions have been performed. In some cases they were not enough to get a reduction of release of the considered compound and the evaluation of the total extractible quantity was not possible ; such situation is mentionned in tables by > of the total of the five extractions.

Results

The following tables 6 to 8 give the results of tests and analyses of the samples extracted from sites A, B, C and D.

Physical properties

TABLE 6

	Site A	Site B	Site C	Site D
Water content %	17	24	16	57
Permeability m/s	$7.9\ 10^{-6}$	$1.2\ 10^{-5}$	$3.4\ 10^{-8}$	$3.8\ 10^{-8}$
Compr. strength daN/cm2	4.7	3.8	1.1	1

TABLE 7 : LEACHING TEST (INSA TEST - FIGURES IN mg kg except pH and conductivity)

Sites A and B

	SITE A		SITE B	
Extract	1	2	1	2
pH	12.7	12.7	12.5	11.1
Conduct ms/m	5.6	5.4	5.3	1.8
COD	2800	2000	3500	6100
TOC	900	490	1440	2040
Cu	6.2	3.7	-	-
Pb	25	21	4.0	
Cd	0.4	0.2	0.4	0.3
Co	<0.5	<0.5	-	-
Va	<0.5	<0.5	-	-
Ni	1.0	0.8	-	-
HC	12	8	11	10
$SO_4^{=}$	-	-	10310	10550
S^-	-	-	11	<0.5

Sites C and D

	SITE C		SITE D	
Extract	1	2	1	2
pH	7.8	7.9	9.6	8.2
Conduct.	0.92	0.49	0.82	0.48
COD	120	60	3200	750
TOC	61	16	1260	260
NH_4	513	108	234	27
Fe	0.8	0.9	0.3	0.6
Cu	<0.5	<0.5	-	-
Zn	0.6	0.5	-	-
P	18	19	-	-
Cr	-	-	0.9	1.1
Ca	-	-	560	410

TABLE 8 : ESTIMATION OF LONG TERM RELEASES

Sites A and B

	SITE A	SITE B
pH	12.7	12.8
Conduct.	5.6	5.8
COD	3200	4760
TOC	1166	1690
Cu	4.8	
Pb	> 10.6	3.26
Cd	> 0.11	>0.12
Co	0.02	-
Cr	0.06	-
Va	0	-
Ni	1.27	-
HC	> 11.8	> 5.9
$SO_4^{=}$		> 5394
S^-		< 0.5

Sites C and D

	SITE C	SITE D
pH	8.5	9.2
Conduct.	0.4	0.44
COD	160	2680
TOC	60	1200
NH_4^+	271	131
Fe	5.1	0.6
Cu	0.06	-
Zn	0.03	-
P	> 4.5	-
Cr	-	< 0.05
Ca	-	315

Problems encountered

The main problem encountered in the field study was the inexistence of reliable data to characterize the initial residues before treatment (except for site B). This fact made impossible any comparison before after treatment in terms of yield. In connection with this problem remains the question of the tests used for the evaluation of treatment efficiency. We can expect to have a standardised .test procedure in France within some months as a result of the research work which is carried on at the present time, but in the scope of the present studies the situation was still not clear. The use of the pressure lixiviation test which is in preparation remained still experimental.

Results

If we consider the laboratory studies, some main results may be mentioned :.

- processes bases on the use of hydraulic cements (like PETRIFIX) are more efficient for the fixation of mineral contaminants than those that use lime as main reagent (like EIF-ECOLOGIE)
- the fixation of the metallic elements needs the maintain of a sufficient pH, not too high, to avoid the release of amphoteric ions. Hexavalent chronium appears however specially difficult to fix
- very good mechanical characteristics can be obtained especially for processes using hydraulic cements

If we consider the field studies :

- we have already mentioned the problems resulting of the inexistence of any reliable characterization of the waste before treatment. One exception is this of site B for which leaching tests (INSA) have been performed before treatment for some parameters with the following results of leachates analysis that can be compared with the results of similar tests of treated wastes made in the recent field study (one extration)

TABLE 9

Parameters	before treatment	after treatment
pH	2.10	12.5
Conductivity ms.m	4.3	5.3
COD mg/kg	52000	3500
sulfates mg/kg	41220	10310

- Although the characteristics of the waste before treatment are not well known, it appears that the TREDI PETRIFIX treatment has not well fixed ammonia (sites C and D) and that release of lead and copper remains important in the case of EIF-Ecologie treatment. This last point is not surprising because of the amphoteric characteristics of these metals and of the high pH of the leachate.

- An other weak point of both treatment applied to the considered sites is their relatively for efficiency in terms of physical characteristics of the treated products. From the consideration of the results of the previous laboratory tests in which this efficiency was much better, it seems that the studied sites treated some years ago had lack of an efficient survey during the treatment operation. It is very probable that these projects were realized with the idea to minimise the expenses.
- Since that time, the applications of these techniques have been improved : the requirement of the authorities in charge of surveying the projects have become more clear and more stringent and the companies are able to propose insurance guaranties of the efficiency of their treatment (evaluated by tests of physical and chemical characteristics) up to twenty years.

Progress will be made by the publication of standardized tests for evaluation of the efficiency of stabilization-solidification processes. This is especially important, not only in the scope of projects of rehabilitation of contaminated sites but also in the view of the use of such techniques for the treatment of ultimate polluting waste, mainly mineral residues of other treatment techniques (incineration).

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IN SITU STABILIZATION/SOLIDIFICATION
OF PCB-CONTAMINATED SOIL

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ABSTRACT

Under the SITE program, a demonstration has been performed on the International Waste Technologies' (IWT) in situ stabilization/solidification process utilizing the Geo-Con deep-soil-mixing equipment. This was the first field demonstration of an in situ stabilization/solidification process. The demonstration occurred in April 1988 at the site of a General Electric Co. electric service shop in Hialeah, Fla., where the soil contained polychlorinated biphenyls (PCBs) and localized concentrations of volatile organics and heavy metal contaminants. The demonstrated process mixed the contaminated soil in situ with a cementitious proprietary additive, called HWT-20, and water.

The technical criteria used to evaluate the effectiveness of the IWT process were contaminant mobility measured by leaching and permeability tests and the potential integrity of solidified soils indicated by measurements of physical and microstructural properties. Performance of the Geo-Con deep-soil-mixing equipment was also evaluated.

The process appeared to immobilize PCBs. However, due to the very low PCB concentrations in the leachates, caused in part by the low concentrations of PCBs in the soils, confirmation of PCB immobilization was not possible. Physical properties were satisfactory except for the freeze/thaw weathering tests, where considerable degradation of the test specimens occurred. The microstructural analyses showed the process produced a dense, homogeneous mass with low porosity, which shows a potential for long-term durability.

The Geo-Con deep-soil-mixing equipment performed well, with only minor difficulties encountered, which can be easily corrected. The HWT-20 additive was well dispersed into the soil, as evidenced by the relatively uniform change in chemical and physical characteristics of treated versus untreated soils.

The estimated remediation cost with operation of the 1-auger machine, used for the demonstration, is \$194/ton (\$150/yd^3). For larger applications, using Geo-Con's 4-auger machine, costs would be lower.

INTRODUCTION

Concern by the public and many government groups exist over using landfills for the containment of hazardous wastes. In response to the Superfund Amendments and Reauthorization Act of 1986 (SARA), the Office of Research and Development (ORD) and the Office of Solid Waste and Emergency Response (OSWER) of the Environmental Protection Agency (EPA) have established a formal program to accelerate the development, demonstration, and use of new or innovative technologies. This program is called Superfund Innovative Technology Evaluation or SITE (1). The major objective of the SITE Program is to develop reliable cost and performance information on innovative alternative technologies, so that they can be adequately considered in Superfund decision making.

The International Waste Technology (IWT) in situ stabilization/solidification process, utilizing their proprietary additive HWT-20, and the injection and deep-soil-mixing technology of Geo-Con, Inc. were evaluated (2). IWT claims that their additive chemically bonds to the contaminants and creates a hardened, leach resistant, concrete-like solidified mass when treating soils containing organics. The demonstration to evaluate the technology was performed at a closed electric service shop in Hialeah, Fla., contaminated with polychlorinated biphenyls (PCBs). In addition, one small area contained volatile organics (VOCs) and low levels of priority pollutant metals. The owner is required by the local regulatory authorities to remediate the site for PCBs. The SITE program demonstration was carried out on two 10x20-ft test sectors selected by the owner and known, from prior soil sampling, to be high in PCBs. The remediation test was performed in April 1988 and lasted six days. Pretreatment soil sampling occurred in March and posttreatment sampling in May 1988. The SITE Program evaluation analyses were performed independently of those required by the local authorities.

PROGRAM OBJECTIVES

The objectives of this SITE Project were to evaluate the IWT/Geo-Con, Inc. in situ stabilization/solidification technology in the following areas:

1. Immobilization of the PCBs in the soil.
2. Effectiveness, performance, and reliability of the Geo-Con deep-soil-mixing equipment used for the in situ solidification.
3. Potential long-term integrity of the solidified soils.
4. Degree of soil consolidation (solidification) produced by the HWT-20 additive.
5. Costs for applying this technology on a commercial scale.

APPROACH

The following technical criteria were used to evaluate the effectiveness of the process:

- Mobility of the contaminants -- Sampling was conducted in areas of high PCBs, the primary contaminant targeted for immobilization, as well as volatile organics and heavy metals, with the analytical emphasis on leaching characteristics. Three leachability tests were performed: the Toxicity Characteristics Leaching Procedure (TCLP) and two leach tests that evaluate performance of the solidified mass, MCC-1P and ANS 16.1, both originally developed for the nuclear industry. Permeabilities were also measured before and after soil treatment. The permeabilities indicate the degree to which the solidified material permits the passage of water through the soil mass, and thus, the degree of water contact with the contaminants.

o Durability of the solidified mass -- Core samples of treated soils were analyzed to determine uniformity and long-term endurance potential. The analyses obtained the following:

  -Integrity of the treated soil.
  -Unconfined compressive strength (UCS), which is an indication of long-term durability.
  -Microstructural characteristics as a source of information on treated soil porosity, crystalline structure, and degree of mixing.
  -Freeze/thaw and wet/dry weathering test data on weight loss; permeability and UCS tests of the weathered samples provided indications of short-term durability.

The stabilization/solidification process utilized the deep soil injection and mechanical mixing equipment of Geo-Con,Inc. A batch mixing system prepared a feed slurry of approximately 57 wt% solids of HWT-20 additive. The slurry was pumped to the injection and mixing auger. Supplemental water was also fed to the auger; the quantity of water was dependent on the moisture content of the soil, i.e., whether the sample was from above or below the water table.

The mixing auger consisted of one set of cutting blades and two sets of mixing blades attached to a vertical shaft rotating at 15 rpm. Two conduits in the hollow auger shaft allowed for the injection of the additive slurry and supplemental water from the base of the auger. HWT-20 was injected on the downstroke, with further mixing occurring upon auger withdrawal.

The soil columns, drilled to a diameter of 36 in., were positioned to provide an overlapping pattern to insure treatment of the entire area. About 25% of each soil column overlapped the other columns.

Two 10x20-ft sectors were treated, each containing 36 soil columns. One sector was treated to a depth of 18 ft and the other to a depth of 14 ft. The depth of injection was determined by the need to treat all soils containing PCBs above 1 mg/kg. The nominal HWT-20 additive rate used was 15 lb of dry additive per 100 lb of dry soil. For the actual demonstration, the additive rates were 0.17 and 0.19 lb/lb dry soil for sectors B and C, respectively.

PROBLEMS ENCOUNTERED

The low quantity of contaminants along with dilution resulting from the soil blending operation caused some difficulties in evaluating the technology. The PCB concentrations in the untreated soil, with the exception of a few points, were below 300 mg/kg, with the largest value measured being 950mg/kg. After soil treatment, due to the mixing of the more highly contaminated soils with soils of lower PCB concentration plus some dilution from the addition of HWT-20 and water, the maximum treated soil concentration was

170 mg/kg, with the remaining samples 110 mg/kg and below. Therefore, due to the low mobility of PCBs, the leachate values were very near the detection limit of PCBs in water of 1.0 ug/L. For a few samples at the end of the analytical program, the PCB analysis procedure was modified to allow measuring to a detection limit of 0.1 ug/L. Even with the increased sensitivity of the analytical method, the ability of the stabilization/solidification process to immobilize PCBs cannot be confirmed by this project.

Only 3 out of 34 sample point locations were found to contain volatile organics (VOCs) and heavy metals. This did not provide a sufficient number of points to evaluate immobilization of these contaminants. In addition, the soil mixing, upon injection of the HWT-20, severely reduced the concentration of the VOCs and metals in the treated soil, further complicating the evaluation.

RESULTS

The results are presented in three parts: immobilization of the contaminants, durability of the solidified mass plus supporting physical tests, and operations of the deep-soil-mixing equipment of Geo-Con.

Mobility of Contaminants

Solidification and stabilization are treatment processes that are designed to accomplish one or more of the following (3):

- Improve the handling and physical characteristics of the waste.
- Decrease the surface area of the waste across which the transfer of contaminants can occur.
- Limit the solubility of hazardous constituents, such as by pH adjustment.
- Change the chemical form of the hazardous constituents, such as by chemical bonding.

Solidification obtains these results primarily by producing a monolithic block of treated waste with high structural integrity. Stabilization techniques limit the mobility of waste contaminants or detoxify them, whether or not the physical characteristics of the waste are changed or improved (4). This is accomplished usually through the addition of materials, such as treated organophilic clays (5) which may provide for chemical bonding, to ensure that the hazardous constituents are maintained in their least mobile form.

For each test sector, pretreatment and posttreatment samples were collected at the same locations. Seventeen samples were collected in each sector. The soil was analyzed for PCBs, and a corresponding TCLP leach test was performed. Therefore, for each leachate concentration measured, the soil concentration was known. Results of treated soils could be compared to those of untreated soils by comparing the quantity of PCBs in the extract to that in the solid specimen being leached--regardless of the fact that localized soil concentrations changed significantly as a result of the soil blending operation.

The maximum PCB concentration measured was 950 mg/kg of untreated soil,with most of the samples under 300 mg/kg. The untreated soil TCLP leachates showed PCB concentrations up to 13 ug/L. Soil samples with PCB concentrations below 63 mg/kg had leachate concentrations below the detection limit of 1.0 ug/L.

All soil samples with more than 300 mg/kg PCBs had measurable leachate concentration. For the untreated soil samples with PCB concentration between 63 mg/kg and 300 mg/kg, only some leachate samples had detectable quantities.

After additive injection and mixing, the maximum treated soil concentration was 170 mg/kg, with all the other samples below 110 mg/kg. All leachates of treated soil samples were below 1.0 ug/L. In addition, seven treated soil leachates from the higher concentration soils were analyzed a second time with detection limits reduced to 0.1 ug/L. Four of the samples were below the revised detection limit. Thus, it appears that the IWT process may immobilize PCBs, but due to the very low values measured, absolute confirmation was not possible. The results from the highest PCB concentration soil samples are provided in Table 1.

Volatile organics, specifically xylenes, chlorobenzenes, and ethylbenzenes, were found in three untreated soil samples with a total concentration up to 1,485 mg/kg. Once the soil was disturbed by the injection and mixing operation, the maximum treated soil total VOCs was reduced to 41 mg/kg. The total VOCs for the untreated soil TCLP leachates was 2.5 to 7.9 mg/L and for the treated soil, 0.32 to 0.61 mg/L. This reduction in VOC concentrations in the leachates is equivalent in order of magnitude to the reduction in VOC concentrations in the soil. Since the VOC concentrations were over a wide range and only three samples were collected, immobilization of the VOCs could not be determined. In addition, IWT claims to have tailored their additive specifically for PCB immobilization.

Heavy metals, primarily lead, copper, chromium, and zinc, were found in only three untreated soil samples, with a maximum total metals concentration of 5,000 mg/kg. After the remediation operation, the heavy metals concentrations in the soil samples were reduced to between 80 and 279 mg/kg. The total metals in the untreated soil TCLP leachate ranged from 0.32mg/L to 12.65 mg/L, and in the treated soil leachate from 0.12 mg/L to 0.21 mg/L. These total metal concentrations are quite low compared to their detection limits and any likely applicable regulatory levels. Due to the limited quantity of data and the low soil concentrations, immobilization of heavy metals could not be determined, although it would be anticipated to occur, since most cementitious processes immobilize heavy metals.

The leachate analyses from leach tests MCC-1P and ANS 16.1 showed all analyte concentrations, PCBs and VOCs, below detection limits. Thus, these tests provided only limited information and did not help in confirming immobilization of PCBs or VOCs.

The permeabilities of the treated soils ranged from 10^{-6} to 10^{-7} cm/s. There was a substantial permeability reduction compared to the untreated soils, which averaged about 1.8×10^{-2} cm/s. Even though the treated soil permeabilities were greater than the EPA guideline value of 1×10^{-7} cm/s, which is targeted for hazardous landfill liners, the four to five order-of-magnitude permeability reduction in treated soil will cause groundwater to flow around, not through, the solidified monolith.

In summary, it appears from the

Table 1. PCBs in soils and leachates.

	PCB Concentrations			
Sample Designation*	Untreated Soil mg/kg	Untreated Soil TCLP Leachate ug/L	Treated Soil mg/kg	Treated Soil TCLP Leachate ug/L
B-6	650	12.0 (15.0)**	49	<1.0 (0.15)**
B-7	460	400.0 (250)**	82	<1.0 (0.12)**
B-8	220	<1.0	9.6	<1.0
B-11	950	7.2 (0.33)**	170	<1.0 (<0.10)**
B-12	140	1.1	16	<1.0
B-13	250	<1.0	---	---
B-16	300	3.7 (0.50)**	100	<1.0 (<0.1)**
B-17	495	3.0 (1.0)**	100	<1.0 (0.2)**
B-21	---	---	60	<1.0
B-22	---	---	114	<1.0
C-1	98	<1.0	20	<1.0
C-3	94	<1.0	57	<1.0
C-7	150	<1.0	22	<1.0
C-10	86	<1.0	80	<1.0 (<0.10)**

* Selected locations of highest PCB concentrations.

** Repeat leachate analysis of existing TCLP leachate analyzed to a detection limit of 0.1 ug/L.

leach tests that PCBs were probably immobilized. In addition, the low permeability of the solidified mass, minimizing water contact with the PCBs, reduced PCB mobility. Nevertheless, PCB immobilization as a result of the IWT/Geo-Con process was not confirmed by the SITE demonstration.

Durability of the Solidified Mass

The ability of the solidified mass to maintain its integrity over a long period of time cannot be determined quantitatively. However, tests were performed that indicated the potential for long-term durability. Unconfined compressive strength provides an indirect measure of structural integrity. The results obtained from the demonstration test ranged from 75 psi to 866 psi and averaged about 410 psi. These values easily exceed the EPA guideline minimum of 50 psi (6). Most other stabilization/solidification processes typically give UCS values in the range of 15 psi to 150 psi (7). Therefore, these results were quite satisfactory.

The effects of weathering can break down the internal structure of the solidified soil potentially producing paths for water flow, which would increase permeability and the potential for contaminant leaching. Wet/dry and freeze/thaw weathering tests were performed. These tests, which involved conditions more severe than exposed solidified material would see in the field, provided an indication of short-term treated soil integrity under natural weathering conditions.

The results for the wet/dry tests showed very small cumulative relative weight losses, averaging approximately 0.1% difference between test specimens and controls. However, the results for the freeze/thaw tests were unsatisfactory, with the cumulative relative weight losses ranging from 0.5% to 30%, and averaging about 6.3%. On a few of the weathered samples, UCS tests were performed. For the wet/dry test specimens, the values obtained were equivalent to the unweathered samples. However, for the freeze/thaw tests, samples with cumulative relative weight losses greater than 3.0% showed reduced UCS values, approaching zero at 10% weight loss. Permeability tests were performed on a few freeze/thaw specimens with weight losses up to 6.0%, with results the same as for the unweathered samples.

Microstructural studies were performed on untreated and treated soil samples. Each sample was studied by scanning electron microscopy, optical microscopy,and x-ray diffraction. Treatment of the contaminated soil produced a dense, homogeneous mass with low porosity. There were no variations in quartz and calcite quantity in the vertical and horizontal directions, even though the original soil was a layered structure. These two sets of observations indicated that the Geo-Con auger provided good mixing for the injection of HWT-20 additive into the soil. These results indicated that the solidified mass has a potential to be highly durable.

Other physical properties of the untreated and treated soils were measured, such as bulk density, moisture content, total organic carbon, and particle size distribution. The bulk density of the soil upon treatment increased 21% as a result of addition of additive plus water of 32 wt%. This resulted in a volume increase of 8.5%. While the volume increase was modest, for a remediation to a depth of 18 ft the ground rise was about 18 in., which could provide land contouring difficulties in many locations. The organics content of the soil was quite low, usually below 0.1 wt%, and would not provide any interferences in the cement hydration reactions. The average of the results for untreated and treated soils are provided in Table 2.

Operations

Equipment performance during the six-day demonstration was smooth, and there were a minimum of operational problems. Each soil column treatment took 30 min. A few operating difficulties were encountered and can be eliminated with some simple engineering design changes. The difficulties were:

- Control of the various flow streams could not be maintained automatically, and manual flow control was needed. This resulted in some uneven additive additions, which with sufficient mixing by the injection auger, did not lead to discernible physical property variations.
- The auger positioning deviated from the targeted point in some locations. This produced areas of poor column overlap, which resulted in areas low in additive.
- Supplemental water addition was lost late in the program as a result of a major leak in the auger header. To save time, operations continued without the supplemental water.

Costs

The IWT/Geo-Con in situ stabilization/solidification system is economical. Remediation costs using the 1-auger machine, used for the demonstration,are \$194/ton (\$150/yd^3). For larger applications, Geo-Con would use its 4-auger machine and costs would be lower.

CONCLUSIONS

The following conclusions can be drawn from the results of the SITE project demonstration:

- PCB do appear to be immobilized by the process. However, due to the very low PCB concentrations in the soil and leachates, it could not be confirmed.
- The physical properties of the treated soil were satisfactory, which would indicate a potential for long-term durability. For each of the test samples, high unconfined compressive strength, low permeability, low porosity, and poor freeze/thaw weathering test results were obtained.
- Operations were well organized and ran smoothly; the difficulties experienced should be readily correctable.

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The analytical services for the physical and chemical tests were performed by NUS Corporation of Pittsburgh, Pa. The microstructural analyses were performed by Louisiana State University (LSU) under the supervision of Scientific Waste Strategies, a consulting organization of professors at LSU.

Table 2. Average soil properties.

	Sector B		Sector C	
	Untreated	Treated	Untreated	Treated
Moisture Content, wt%	11.8	19.0	13.2	17.3
Bulk Density, g/mL	1.51	1.85	1.56	1.94
Permeability, cm/s	$1.46\text{x}10^{-2}$	$5.5\text{x}10^{-7}$	$3.5\text{x}10^{-2}$	$2.7\text{x}10^{-7}$
Unconfined Compressive Strength, psi	--	290	--	536
Weathering Tests				
Wet/Dry, wt% lost	--	0.39*	--	0.34*
Freeze/Thaw, wt% lost	--	7.2*	--	6.0*
pH	8.1	--	8.5	--
Oil and Grease, wt%	0.3	--	0.1	--
TOC, mg/kg	4,380	--	2,300	--

* These values represent the weight loss of the test specimens. The wet/dry weight losses of the controls were approximately 0.1% less. For the freeze/thaw controls, the absolute weight losses were in the range of 0.3% to 0.4%.

The authors wish to express their appreciation for the services provided.

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

APPLICATIONS OF GEOPOLYMER TECHNOLOGY TO WASTE STABILIZATION

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ABSTRACT

Hazardous wastes can be rendered innocuous through chemical (waste stabilization) or physical (waste encapsulation) methods. A research program has been conducted at D. Comrie Consulting Ltd. in order to evaluate geopolymer as an agent for both waste stabilization and encapsulation.

Physical properties of solidified waste and sand mortar mixes have been examined on the basis of compressive strength testing. Abilities of geopolymer to render waste chemically innocuous have been assessed on the basis of leachate testing carried out in accordance with Ontario's Ministry of Environment Regulation 309 guidelines.

Preliminary results show this inorganic binder as extremely effective in reducing metal leachability in a wide range of wastes, and that the physical properties of solidified products make it an ideal candidate for waste stabilization or encapsulation.

INTRODUCTION

Waste treatment can be effected through both physical and chemical processes. Waste treatment and stabilization may be carried out either independent of, or in conjunction with physical encapsulation. While chemical treatment may render the waste itself essentially chemically inert and no longer susceptible to releasing toxins in response to leaching, physical encapsulation concentrates on isolating the waste from interaction with surrounding surface and groundwater.

There are many stabilization agents available for the treatment of toxic waste. Testing of these materials has met with varying degrees of success at reducing the leachability of contaminants in the waste. The purpose of this research program was to evaluate the performance of one such stabilization agent - an inorganic binder known as geopolymer.

GEOPOLYMERS

Geopolymers are inorganic binders consisting of two components: a very fine and dry powder, and a syropy, highly alkaline liquid. Liquid and powder portions are combined to produce a mixture of molasses-like consistency which is then reacted with the desired waste or aggregate. Blending of the two binder components can be readily carried out with the aid of conventional cement mixing technology. The resulting waste-binder mixture can be poured into molds (for example, fibre drums such as might be obtained from a concrete products supplier); drier mixes have potential for extrusion.

The geopolymeric reaction occurs as a result of reacting alumino-silicate oxides with alkali (NaOH, KOH) and soluble alkali polysilicates. Resulting from this reaction is the formation of SiO_4 and AlO_4 tetrahedra linked by shared oxygens. A mildly exothermic reaction in the alkali activated mixture is accompanied by hardening and polycondensation.

The basis of the sialate (or, silicon-oxo-aluminate) network of SiO_4 and AlO_4 tetrahedra is illustrated in Figure 1. Positive ions, such as sodium, potassium, lithium, calcium or barium, must be present in the framework cavities in order to achieve charge balance.

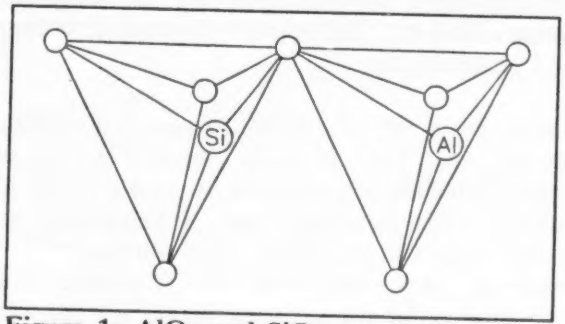

Figure 1: AlO_4 and SiO_4 tetrahedra - basis of the sialate network.

PHYSICAL CHARACTERISTICS

Geopolymers are characterized by a number of interesting physical characteristics, including thermal stability, high surface smoothness, precise moldability and hard surfaces (4-7 on Moh's scale) (Davidovits and Davidovits, 1987). These properties are commonly imparted to products created through a combination of binder with waste materials. In terms of waste stabilization or encapsulation, the most significant physical property imparted by geopolymers is their ability to transform soft, disaggregated or sludge-like wastes into hard, cohesive solids in remarkably short time frames.

Physical testing has been carried out on unconfined cubes created from mortar mixes of sand and geopolymer. Compressive strengths of 40 MPa have been achieved over a 28 day cure period; strengths of 30 MPa (75% of final strength) are acquired in the initial two days of curing (Figure 2). Strengths are acquired with considerable speed in comparison to mortars developed from regular Portland cement (Figure 3).

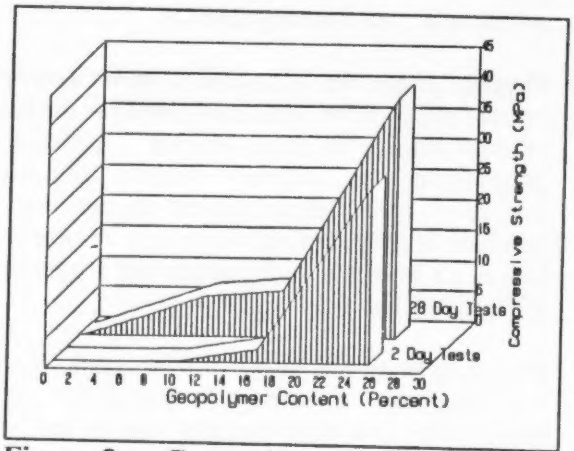

Figure 2: Comparison of 2 and 28 day strengths in inorganic binder based mortars.

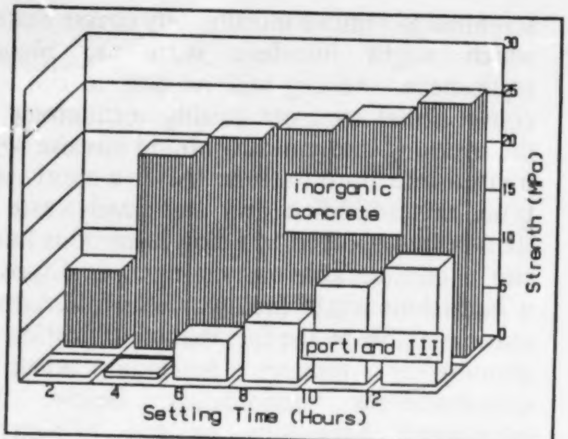

Figure 3: **Comparison of Normal Portland and Inorganic Binder Based Concrete Initial Strengths.**

In fact, some inorganic binders have been developed to form solid, cohesive masses within one to two minutes of mixing with aggregate or waste forms. Of course, compressive strengths achieved depend on the nature of the aggregate or waste form employed in conjunction with the binder, and the amount of binder used.

CHEMICAL CHARACTERISTICS

In addition to their physical properties, geopolymers are characterized by an ability to resist chemical attack. This is attributed to the fact that, unlike cements, lime does not play a part in the lattice structure which provides the structural strength to the product. The resistance provided against chemical attack is best illustrated by the ability of geopolymer to retain toxins during acidic leaching.

In order to examine this property, a variety of toxic waste samples have been collected from different waste generators. Each sample was split into three and the first portion was assayed for metal concentrations. The second portion was subjected to leachate testing in accordance with Ontario's Ministry of the Environment Regulation 309, Schedule 4 guidelines, calling for pulverization of the sample followed by tumbling in acetic acid. The third portion of each waste was treated with geopolymer and, after curing for 7 days, leach tested. Results were compared with the maximum permissible leachate concentrations allowed by the Ministry of Environment.

Tests conducted on waste at a southern Ontario scrap yard have proved most successful. Bulldozer and soil movement operations at the scrap yard, which has been used for crushing and compacting both automotive and industrial scrap, have resulted in contamination which extends approximately 2 meters down into the soil. Of prime concern is lead contamination, resulting from scrapped car batteries. Analysis of soil from the yard indicates lead concentrations in the order of 6,000 ppm, with 25.3 mg/l leaching out during Regulation 309 style tests. In contrast, samples treated with a geopolymeric inorganic binder leached out only 2.1 mg/l, well below the Ministry of Environment limit for safe emissions of 5 mg/l.

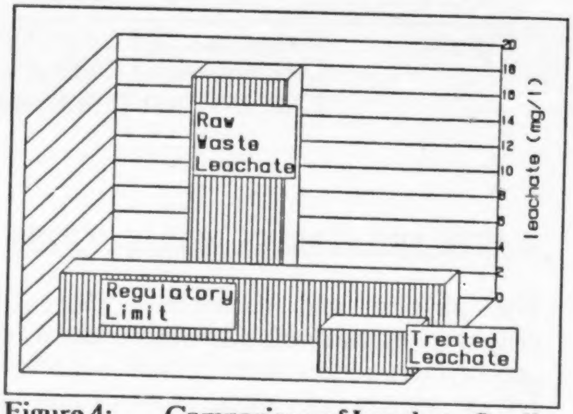

Figure 4: **Comparison of Leachate Quality in Treated and Untreated Scrap Yard Waste.**

Similar tests were conducted on contaminated soils surrounding a southern Ontario refining and smelting operation. A series of leaks and spills during the plant's forty year operational life have resulted in lead contamination to a depth of three meters. Concentrations of lead in the soil average about 285,000 ppm, with 204 mg/l released to leachate during Regulation 309 style leaching. Geopolymerization brings this level down by an order of magnitude, to 18.3 mg/l.

Figure 5 illustrates the effect on leachate quality as a result of increasing geopolymer content. Ore processing waste (tailings) from an Ontario base metal mining operation was solidified with 10, 15 and 25 weight percent geopolymer.

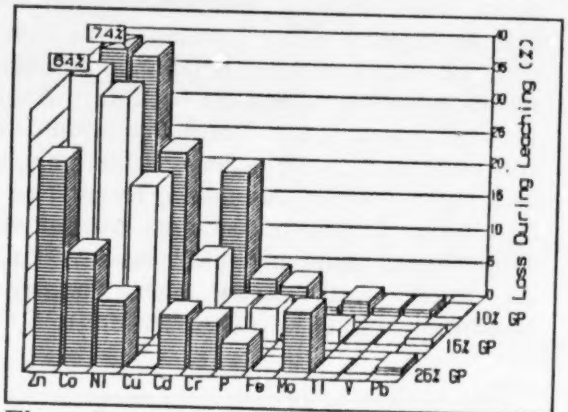

Figure 5: Comparison of % Loss During Leaching - Mine Tailings with 10%, 15% and 15% Binder.

WASTE TREATMENT APPLICATIONS

The physical and chemical properties of geopolymers and of products created with geopolymers makes them attractive candidates for a variety of waste stabilization and encapsulation situations (Comrie, 1988; Comrie and Davidovits, 1988; Davidovits and Comrie, 1988). The automotive scrap yard and the refining and smelting operation noted above represent good examples of possible applications.

Work has already been initiated at the automotive scrap yard on a pilot plant (20 tonne) scale, and contaminated soil has been screened to remove inordinately coarse material which might interfere with the blending equipment. Mixing will be carried out using conventional concrete mixing technology, and the resulting inorganically bound mixture will be poured into fibre barrels. After a short curing time, this solidified and stabilized waste can then be transported to a non-hazardous landfill site, at considerable cost savings over disposal at a hazardous waste facility. This alternative is made possible by the fact that solidification with geopolymer reduces leachate levels to concentrations significantly below those considered hazardous by the Ministry of Environment in Ontario.

Plans for remediation of the refining and smelting site noted above call for a combination of chemical waste stabilization and waste encapsulation. The most contaminated area on the site will be excavated to create an empty "vault", with the removed soil stored nearby. While the vault is lined with low permeability, high strength geopolymer concrete, the soil set aside will be treated with geopolymer to create a solid of minimal leachate hazard. The treated soil will then be returned to the vault and capped with 100 mm of geopolymer concrete, on top of which will be placed an additional 600 mm of top soil. The entire perimeter of the vault will be surrounded with peripheral surface water ditches, resulting in a waste management unit which contains a waste of minimal reactivity and which is isolated from interaction

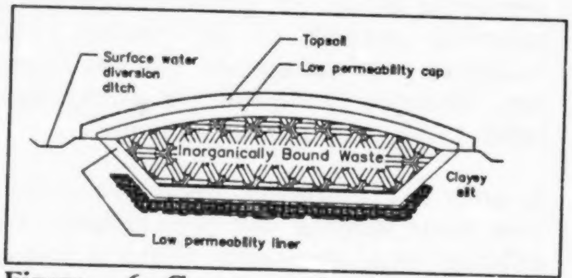

Figure 6: Cross-section of Waste Management Unit for Treatment of Smelter Yard Waste.

with ground and surface water (Figure 6).

The unique properties of geopolymer and inorganic binders, including rapid achievement of high strengths and the ability to immobilize chemical toxins even under conditions of acidic leaching, should result in some interesting future applications.

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INVESTIGATION OF STABILIZING ARSENIC-BEARING SOILS AND WASTES USING CEMENT CASTING AND CLAY PELLETIZING/SINTERING TECHNOLOGIES

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ABSTRACT

Cement casting and clay pelletizing and sintering are two treatment techniques for hazardous wastes containing toxic metals. Research in the past has indicated these techniques may be effective in stabilizing arsenic wastes. Treatability studies using these techniques were conducted on arsenic-bearing soils and wastes present at the Whitmoyer Laboratories Superfund Site.

Treatability study results are presented. The experimental results revealed that cement casting was somewhat effective in stabilizing a calcium-arsenic sludge. Stabilization was enhanced by incorporation of a pre-roasting step prior to hydration or by thiourea addition.

Cement casting was not effective in fixing the arsenic in an iron-arsenic sludge and a sludge/soil mixture. However, pre-roasting the cement-waste combination prior to hydration was effective in promoting waste stabilization.

Clay pelletizing and sintering was partially successful in stabilizing the calcium-arsenic sludge. This technology was not effective on the iron-arsenic wastes, however. In all cases, significant quantities of arsenic volatilized during treatment.

INTRODUCTION

The Whitmoyer Laboratories Superfund Site is located in Jackson Township, Lebanon County, Pennsylvania. Veterinary pharmaceutical products, including organic arsenicals, were manufactured at the site. Prior to 1964, the site operators treated arsenic-bearing wastewater by adding lime to effect arsenic precipitation in an unlined lagoon. When environmental consequences from this practice were noted, the sludge was excavated and placed into a concrete vault, where it currently resides (2). An estimated 2,000 tons of sludge ("vault sludge") containing 370 tons (740,000 pounds) of arsenic were placed into the vault. Other site wastes, including organic chemicals, were also placed in the vault. These other wastes have partially mixed with the sludge. There are concerns about the vault's structural integrity.

The site operator conducted a groundwater pump-and-treat program at the site from 1964 to 1971. During this period arsenic-bearing groundwater was extracted and treated with ferric sulfate and lime to precipitate an iron-arsenic sludge in two sets of lagoons.

In 1976-1977, the site operator excavated the iron-arsenic sludge from one set of lagoons and placed this sludge on top of the sludge present in the other lagoons. To improve the sludge's bearing capacity, soils were added to the sludge. Thus, there are two distinct sludge materials present in these "consolidated lagoons": a relatively pure sludge ("lagoon sludge"), overlain by a mixture of sludge and soil ("sludge/soil mixture"). An estimated 4,000 cubic yards of lagoon sludge and 10,000 cubic yards of sludge/soil mixture are present in the consolidated lagoons.

At the time the vault and lagoon sludges were generated, they were believed to be environmentally stable. Recent research (9,10) has shown, however, that these precipitates leach an environmentally-significant amount of arsenic. There is a concern that the sludges are contributing to soil, ground- and surface-water contamination at the Whitmoyer site.

PURPOSE

The Superfund Amendments and Reauthorization Act of 1986 (SARA) requires the U.S. Environmental Protection Agency (USEPA) to use treatment technology to the maximum extent practicable for remediation of Superfund wastes. To achieve this goal on the Whitmoyer sludge wastes, a technical memorandum evaluating the applicability of treatment technologies was prepared (1). Based on cost, potential effectiveness, and implementability, two technologies, cement casting (with and without a pre-roasting step) and clay pelletizing and sintering, were recommended for further consideration as treatment technologies. Since these technologies were unproven on the Whitmoyer wastes, bench-scale treatability studies were initiated.

APPROACH

Background-Cement Casting

Research by Mehta (7) has indicated that pure calcium arsenate, ferric arsenate, and arsenic trioxide can be stabilized (as defined by a distilled water leaching procedure) by binding the arsenic in a cement matrix. The efficacy of the cement casting technology on other forms of arsenic (iron and calcium arsenites and organically-bound arsenic) was not investigated by Mehta. Johnson and Lancione (3) tested fourteen proprietary and nine generic fixation processes on residues from the production of arsenical herbicides (organic arsenicals). They reported that all of the samples of treated herbicides released between 28% and 100% of their arsenic when subjected to a distilled water leach (after crushing). Lopat Enterprises, Inc. (6) chemically fixed three soil samples from the Vineland Chemical Company Superfund Site (herbicide manufacturing plant) using mixtures of activated carbon, cement, fly ash, lime and their proprietary ingredient "K-20 LS." All of the samples leached less than 0.36 mg/l arsenic when analyzed using the USEPA RCRA Extraction Procedure (EP) Toxicity test. (USEPA defines a RCRA characteristic hazardous waste for arsenic as one with an EP extract above 5.0 mg/l.) Tetsuro and Matsunaga (12), as cited in Kawashima et al. (4), reported that arsenic-containing sludges can be treated with a 5% aqueous solution of thiourea, sand and portland cement to create a concrete with arsenic leachate levels "far below regulation levels."

Mehta (7) demonstrated that the arsenic solubility of the arsenic-cement mixtures could be lowered even further by pre-roasting the mixtures at 600°C prior to casting and curing. This reduction in solubility could be due to the dehydration-crystallization effects discussed below.

Nishimura and Tozawa (8) reported that a crystalline, anhydrous calcium arsenate with limited arsenic solubility could be created by calcining pure calcium arsenate and calcium arsenite above 700°C. Nearly all of the arsenite was oxidized to arsenate at roasting temperatures above 600°C. Stefanakis and Kontopoulos (11) confirmed Nishimura and Tozawa's work. Wenshao (14) reported that this calcination process was effective on an industrial calcium arsenate sludge.

Tozawa et al. (13) demonstrated that calcining pure ferric arsenate above 600°C reduced the arsenate's solubility in the pH range of 2-7 by forming crystalline, anhydrous ferric arsenate. However, above 800°C, the ferric arsenate thermally decomposed to a more soluble compound. Also, at this temperature, a significant amount of arsenic was volatilized.

Background Clay Pelletizing and Sintering

The second recommended technology, clay pelletizing and sintering (roasting to form a coherent mass), was shown by Mehta to be effective in stabilizing pure calcium arsenate, iron arsenate, arsenic trioxide, and arsenic pentoxide (7). The treated arsenic trioxide and pentoxide typically leached arsenic in distilled water in concentrations above 5 mg/l; however, this level is much lower than their untreated arsenic solubilities in water. The iron and calcium arsenate leachate concentrations were all below 0.3 mg/l.

The effects of impurities, specifically organics and soil, and other arsenic forms on the clay mixtures have not been investigated in the past.

Testing Program and Methodology

To evaluate the efficacy of the cement casting technology, 42 experiments were conducted on the three arsenic wastes. Each test's conditions (as well as the test's results) are presented in Tables 2 to 4. Key testing variables included cement/waste ratio, lime/waste ratio, incorporation of a pre-roasting step prior to hydration, roast temperature, and cure time. All wastes were air-dried and milled (to break up chunks) prior to treatment initiation. Wastes and additives were mixed in a rolling mill. When conducted, roasting generally occurred in a muffle furnace; roasting for tests 5-14 for the vault waste and 5-8 for the lagoon sludge took place in a tube furnace. Mixtures were roasted for 1 hour at the designated temperature. Between 28% and 48% water was added to the mixtures during hydration. Cast samples were cured at 22°C (70°F) and 100% humidity.

Clay pelletizing and sintering was tested at two ratios, 3:1 clay/waste and 1:3 clay/waste. Wastes were air dried and milled to break up chunks; bentonite clay was added, and the mixtures blended in a rolling mill. The mixtures were pelletized in a disk pelletizer and then sintered at 1,000°C. Test conditions (and results) are presented in Table 5.

To measure the success of the treatment tests, three leachate procedures were used: the USEPA Toxicity Characteristic Leaching Procedure (TCLP), which uses acetic acid as an extractant; a modified ASTM leachate procedure (Method D3987-85) where the same treated sample is extracted for 2 days in fresh distilled water three times, with each extract being analyzed separately; and a second modification of the ASTM leachate procedure with identical conditions to the previously-described test, except 3 g/l $NaHCO_3$ solution is used instead of distilled water. All three test procedures require a 20:1 liquid/solid ratio.

The TCLP procedure is used by the USEPA to determine if a hazardous waste needs treatment (or additional treatment) prior to land disposal.

Krause and Ettel (5) demonstrated that iron arsenate is more soluble at neutral and alkaline pHs than at pHs less than 5. The modified ASTM distilled water leaching procedure was selected to test treated product leachability with neutral extractant.

Work by Robins and Tozawa (10) and Nishimura et al. (9) indicated that, in the long term, calcium arsenate and arsenite are decomposed by carbon dioxide to calcium carbonate, releasing arsenic acid. There is a concern that cement-waste matrices may be attacked by atmospheric carbon dioxide (CO_2), CO_2 dissolved in rain water, and carbonate derived from mineral leaching, resulting in decomposition and arsenic release. To evaluate this possibility, the bicarbonate leaching procedure was developed. This process also serves to test the leachability of the treated products under alkaline conditions.

The project team set a primary treatment objective of 1.0 mg/l leachable arsenic for each of the three leachate procedures. A secondary objective of a 90% reduction in total organic carbon leachability was set, using the two non-acetic acid based leachate procedures. This secondary objective was only applicable if significant organics were detected in the wastes.

RESULTS

Waste Characterization

Initial analyses of the untreated waste samples are presented in Table 1. As can be seen, the vault sludge has insufficient calcium to effectively bind the arsenic as calcium arsenate or arsenite. The Ca/As molar ratio is 0.92:1, which is significantly less than the stoichiometric ratios of 1:1 and 2:1 required to form calcium arsenite• and calcium arsenate•calcium hydroxide, respectively (11). The vault sludge's iron and magnesium content are relatively small. Thus, a significant portion of the vault sludge's arsenic is either present as a sodium-arsenic compound, organically-bound arsenic, or in some other soluble form. The untreated vault sludge's distilled water leachate contained 1,650 mg/l arsenic, 851 mg/l arsenic, and 512 mg/l arsenic for the three extractions (see Table 2). The quantity of arsenic leached from the sample during the three extractions was 38% of the arsenic present. This supports the contention that much of the arsenic in the vault sludge is present in a readily soluble form.

The initial analyses for the lagoon sludge and sludge/soil mixture are also shown in Table 1. The Fe/As ratios for both the lagoon sludge and the sludge/soil mixture were both greater than 4:1. Thus, there probably is sufficient iron in the samples for the arsenic to be bound in iron-arsenic compounds. This is supported by the samples' limited arsenic leachability as shown in Tables 3 and 4. Calcium is also abundant, although it may be bound to sulfate ions.

Cement Fixation

Cement casting (without a pre-roasting step) reduced the vault sludge's TCLP leachate concentration by a minimum of 91% (99.8% for the 3:1 cement sample mixture -28 day cure). Significant reductions in the sludge's distilled water leachate concentration were also noted. The TCLP leachate concentration of the 3:1 cement mixture was an order of magnitude lower than the 1:1 cement mixture's concentration.

Cement casting without pre-roasting increased the lagoon sludge and sludge/soil mixture's leachate arsenic concentrations in all cases. This phenomenon may be due to the increased solubility of iron-arsenic compounds at pHs above 5 (5). The cement addition resulted in solution pHs above 9. Arsenic concentrations in the leachate decreased with increasing cement/waste ratios.

Pre-Roasting

Pre-roasting reduced the leachate arsenic TCLP and distilled water concentration of the vault-cement mixtures by an additional one to two orders of magnitude beyond that of cement fixation only; leachate concentrations were reduced by approximately two orders of magnitude for the cement-lime-waste mixtures. Greater reductions in leachate concentrations were generally achieved at higher Ca/As ratios. TCLP and distilled water leachate concentrations as low as 0.99 mg/l and 0.15 mg/l arsenic were achieved for the vault waste. Between 0% and 7% of the arsenic was volatilized during the roasting step.

Cement casting with pre-roasting for the lagoon sludge and sludge/soil mixture similarly was successful in reducing the TCLP and distilled water leachate arsenic concentrations (except for the 1:5 cement/waste mixture).

To differentiate the importance of the roasting step from the cement casting step, a series of tests (vault waste tests 5-14 and lagoon sludge tests 5-8; see Tables 2 and 3) were conducted where the wastes and waste fixative mixtures were roasted but not cast (hydrated). For the vault wastes, TCLP leachate arsenic concentrations approached levels reached for the roasted, cast, and cured samples only when the mixtures were roasted and excess calcium was added. This indicated that the anhydrous calcium arsenate with limited arsenic solubility described by Nishimura and Tozawa (8) may have been formed during roasting. Roasting temperature increases above 600°C had little effect on the TCLP leachate arsenic concentration. Since the lagoon sludge had Fe/As molar ratios greater than 4:1, roasting without additives was conducted at temperatures between 600°C and 1,000°C to see if the low arsenic solubility, anhydrous ferric arsenate described by Tozawa et al. (13) could be created. These tests were not successful, as up to

12% of the arsenic volatilized at the higher temperatures and the products' TCLP leachate arsenic concentration were greater than the concentration for the untreated sludge.

The mechanism for the increased stabilization achieved for the iron-arsenic sludges from roasting is not readily apparent.

Lime Addition

Lime addition to the cement-vault waste mixture without pre-roasting did not discernably enhance arsenic stabilization. However lime addition with pre-roasting significantly reduced the TCLP and distilled water extracts' arsenic concentration. This phenomenon occurred even when cement was not added to the waste mixture and the mixture was not hydrated (see Table 2, experiment No. 14). As mentioned above, the arsenic stabilization may be due to the formation of calcium arsenate.

Thiourea Addition

When 5% thiourea (by weight) was added to the 1:1 cement-vault sludge mixture a tenfold reduction in the arsenic TCLP leachate concentration was noted. However, when 1% thiourea (by weight) was added to the 1:1 cement-sludge mixtures, no appreciable reduction was identified.

Cure Time

TCLP leachate arsenic concentrations were measured after both 5 and 28 days of curing. When the 5-day TCLP leachate arsenic concentration was greater than 10 mg/l, a significant reduction in the arsenic concentration was noted for the 28-day samples. However, when the 5-day concentration was less than 10 mg/l, no further reduction was achieved.

Effect of Carbonate and Cement Casts, Samples

The cement-waste matrices were attacked by the aggressive bicarbonate leaching solution. In all cases, the $NaHCO_3$ extracts contained more arsenic than either the TCLP or distilled water extracts. The $NaHCO_3$ effect was most pronounced on the roasted samples. By the third extraction, the leachate arsenic concentration approached the concentration for the unroasted samples, i.e., the $NaHCO_3$ solution negated the additional stabilization provided by roasting.

Clay Pelletizing and Sintering

The clay pelletizing and sintering technology was moderately successful with the vault sludge. The arsenic leachate concentration (TCLP) was reduced by a minimum of 95%. However, between 11% and 33% of the arsenic was volatilized during sintering.

The clay pelletizing and sintering technology was not successful on the lagoon sludge and sludge/soil mixture samples. The arsenic leachate concentrations increased by an order of magnitude after treatment, and between 20% and 80% of the arsenic volatilized during sintering.

The clay pelletizing and sintering technology failed to meet the project treatment objectives. Two possible reasons for this failure are that the organic content of the samples caused reducing conditions during sintering, resulting in arsenic trioxide formation and volatilization, and that excess iron in the samples reacted with iron-arsenic compounds to form $Fe_2O_3 \cdot 2FeAsO_4$, with accompanying arsenic volatilization. This iron-arsenic compound was noted by Tozawa et al. (13) to form above 800°C, and is more soluble than basic ferric arsenate.

Conclusions

Cement casting was somewhat effective in stabilizing the calcium-arsenic (vault) sludge. Additional stabilization was provided by incorporating a pre-roasting step prior to hydration. Thiourea addition to the cement-waste mixture appeared to enhance stabilization of the vault waste.

Cement casting was not effective in fixing the iron-arsenic lagoon sludge and sludge/soil mixture. However, cement casting combined with a pre-roasting step effectively stabilized these wastes.

Bicarbonate leach test results indicate that carbonate derived from atmospheric carbon dioxide, infiltrating rainwater and/or limestone immediately underlying the site may attack cement-stabilized wastes over time. If this technology is selected for remediation, the treated waste landfill must be designed to counter this effect.

Clay pelletizing and sintering does not appear to be well suited to the Whitmoyer wastes. This technology did not meet the treatment objectives for stabilizing the wastes.

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DISCLAIMER

This material has been funded wholly or in part by the Environmental Protection Agency under Contract Number 68-01-7250 to Ebasco Services, Inc. It has been subject to the Agency's review, and it has been approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

TABLE 1

UNTREATED WASTE CONTAMINANT CONCENTRATIONS
(mg/kg unless otherwise indicated)

	Vault Sludge	Lagoon Sludge	Sludge/Soil Mixture
Aluminum	10,700	9,800	15,500
Antimony	480	14	<12
Arsenic	157,000	36,000	22,000
Barium	<120	46	101
Beryllium	<40	1.5	1.6
Cadmium	<6	16	10
Calcium	72,400	100,000	60,000
Chromium	43	16	22
Cobalt	<20	23	22
Copper	42	134	105
Iron	6,900	110,000	69,000
Lead	62	710	300
Magnesium	2,060	22,200	40,000
Manganese	227	195	830
Mercury	<0.3	0.15	<0.2
Nickel	<40	25	29
Potassium	<5,000	1,200	910
Selenium	<20	2.8	0.6
Silicon	29,800	NA	NA
Silver	<40	1.4	0.5
Sodium	67,000	<1,000	<1,000
Thallium	<400	<2	0.8
Titanium	930	NA	NA
Vanadium	<200	14	19
Zinc	<40	150	130
Total Organic Carbon (%)	1.01	0.56	0.33
Sulfate	3,200	11,800	11,300
Aniline	2,000	<0.3	<0.3

NA = Not Analyzed

TABLE 2

ANALYTICAL RESULTS
VAULT WASTE TREATED BY CEMENT CASTING

Exp. No.	Cement: Sludge Ratio	Lime: Sludge Ratio	% Thiourea (Total Weight)	Roast Temp (°C) (60 min)	Cure Time (days)	Ca/As Ratio	% As Volatilized	TCLP Leachate Results		Distilled H_2O Leach 1st Extract			Distilled H_2O Leach 2nd Extract			Distilled H_2O Leach 3rd Extract			$NaHCO_3$ Leach 1st Extract			$NaHCO_3$ Leach 2nd Extract			$NaHCO_3$ Leach 3rd Extract			Unconfined Compressive Strength (psi)
								As mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	
0	---	---	---	---	---	0.86	---	2260	7.0	1650	1019	8.6	851	414	8.5	512	166	9.0	2060	1008	8.7	2710	659	10.4	1900	226	10.7	---
1	3	---	---	---	5	5.7	---	33	11.8	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
1	3	---	---	---	28	5.7	---	5.4	11.6	50.2	66.6	12.4	21.4	34.3	12.4	22.6	46.5	12.6	98.5	62.9	12.9	91.9	28.4	12.4	113	34.7	12.3	4340
2	3	---	---	600	5	5.7	6.4	9.65	11.5	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
2	3	---	---	600	28	5.7	6.4	0.99	11.7	1.27	3.07	12.4	0.45	7.21	12.4	0.39	28.3	12.5	25.9	4.9	12.9	70.7	6.06	12.4	76.1	14.2	12.4	5390
3	1	---	---	---	5	2.2	---	200	11.5	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
3	1	---	---	---	28	2.2	---	72.2	11.4	197	243	12.4	57.1	74.5	12.4	49.9	52.1	12.4	284	257	12.9	180	66.3	12.3	200	51.7	12.2	2300
4	1	---	---	600	5	2.2	2.7	3.22	11.2	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
4	1	---	---	600	28	2.2	2.7	10.8	10.3	0.85	1.5	12.3	0.49	3.5	12.4	0.83	20.0	12.4	61.5	2.0	12.9	83.8	7.53	12.4	117	17.7	12.2	2230
5	---	---	---	600	---	0.86	26	2291	5.8	---	---		---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
6	---	---	---	700	---	0.86	37	1546	5.6	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
7	---	---	---	800	---	0.86	42	1213	5.6	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
8	---	---	---	1000	---	0.86	86	347	6.0	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
9*	---	1	---	---	---	9.3	---	578	12.9	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
10*	---	1	---	700	---	9.3	<1	1.6	12.9	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
11*	3	---	---	---	---	5.7	---	333	12.4	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
12*	3	---	---	600	---	5.7	9.3	2.2	11.8	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
13*	3	---	---	700	---	5.7	9.2	1.2	11.8	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
14*	3	---	---	800	---	5.7	<1	1.8	12.4	---	---	---	---	---	---	---	---	---	---			---	---	---	---	---	---	---
15	1	---	5	---	3	2.2	---	20	8.0	---	---	---	---	---	---	---	---	---	---	---		---	---	---	---	---	---	---
16	1	---	1	---	28	2.2	---	93.1	11.6	287	423	12.3	109	110	12.2	63.9	57.0	12.3	414	424	12.2	16.7	86.0	12.1	20.3	50.1	12.0	1510
17	1	1	---	---	28	1.1	---	82.3	11.9	244	295	12.0	66.5	73.0	11.3	32.1	41.1	12.5	283	332	12.3	76.4	78.9	12.4	51.3	569	12.2	880
18	1	1	---	700	28	1.1	0	1.3	11.9	0.15	2.75	12.0	0.10	13.3	12.3	0.20	10.5	12.5	0.95	1.41	12.2	5.41	2.34	12.3	49.4	5.85	12.1	1080
19	0.7	0.6	---	---	---	7.0	---	102	12.0	257	295	12.1	63.3	76.5	12.2	32.1	39.9	12.6	295	324	12.3	98.7	96.0	12.3	178	41.0	12.1	520
20	0.7	0.6	---	700	---	7.0	3.8	1.84	11.85	0.67	3.21	12.1	0.29	11.8	12.3	0.28	9.95	12.5	1.22	2.52	12.3	15.6	3.42	12.3	127	5.13	12.0	---

* Uncast cement samples
Blank Results pending
--- Not analyzed or reagent not added

TABLE 3

ANALYTICAL RESULTS
LAGOON SLUDGE TREATED BY CEMENT CASTING

Exp. No.	Cement: Sludge Ratio	% Thiourea (Total Weight)	Roast Temp (°C) (60 min)	Cure Time (days)	% As Volatilized	TCLP Leachate Results		Distilled H_2O Leach 1st Extract			Distilled H_2O Leach 2nd Extract			Distilled H_2O Leach 3rd Extract			$NaHCO_3$ Leach 1st Extract			$NaHCO_3$ Leach 2nd Extract			$NaHCO_3$ Leach 3rd Extract			Unconfined Compressive Strength (psi)
						As mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	
0	---	---	---	---	---	4.62	6.1	5.03	10	7.6	4.88	8.5	7.6	1.86	6.6	8.4	10.5	17.5	8.9	126	232	10.6	101	208	10.8	---
1	3	---	---	5	---	6.71	11.5	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
1	3	---	---	28	---	5.02	11.5	20.5	6.76	12.3	2.65	4.71	12.1	2.58	11.2	11.9	10.5	9.31	12.8	11.0	10.2	12.5	0.91	18.3	12.3	8380
2	3	---	600	5	---	0.18	11.5	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
2	3	---	600	28	---	0.11	11.7	0.10	1.54	12.3	0.07	6.81	12.3	0.08	16.0	11.9	1.45	3.36	12.9	5.79	6.04	12.4	11.4	16.7	12.4	8060
3	1	---	---	5	---	38.7	11.4	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
3	1	---	---	28	---	15.8	11.0	20.0	26.5	12.3	9.90	11.6	12.1	9.92	11.7	12.1	27.3	28.3	12.7	22.9	28.8	12.3	27.1	24.8	12.2	5580
4	1	---	600	5	---	0.19	11.5	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
4	1	---	600	28	---	0.43	11.5	0.12	1.73	12.3	0.07	1.5	12.2	0.03	3.61	12.0	0.73	1.22	12.8	19.0	6.06	12.4	39.2	16.3	12.2	6010
5	---	---	600	---	<1	344	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
6	---	---	700	---	<1	106	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
7	---	---	800	---	5.9	22.7	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
8	---	---	1000	---	11.9	10.8	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
9	0.5	---	---	28	---	399	11.6	56.6	51.7	12.2	19.0	24.7	12.1	7.70	17.9	12.1	58.9	54.8	12.3	24.9	29.4	12.1	49.1	23.0	11.9	---
10	0.5	---	700	28	5.8	0.45	11.5	0.08	2.13	12.1	0.03	7.18	12.2	0.04	7.55	12.1	0.20	3.29	12.3	2.15	2.50	12.1	21.0	5.13	12.0	3590
11	0.2	---	---	28	---	36.4	9.7	67.0	60.2	11.9	10.3	20.4	11.9	4.18	9.25	11.9	66.2	73.9	11.9	105	41.4	11.8	53.3	26.7	10.1	2110
12	0.2	---	700	28	0	17.5	9.5	0.25	3.29	11.8	0.13	3.94	11.9	0.09	4.34	11.9	0.87	4.47	11.9	36.5	2.21	11.9	66.4	2.85	10.8	2790
13	1	1	---	28	---	18.8	11.6	22.6	221	12.1	7.37	35.7	12.3	6.20	17.7	12.4	24.5	236	12.2	14.8	37.7	12.2	25.0	18.5	12.0	---

* Uncast cement samples
Blank Results pending
--- Not analyzed or reagent not added

TABLE 4

ANALYTICAL RESULTS
SLUDGE/SOIL MIXTURE TREATED BY CEMENT CASTING

Exp No	Cement Sludge Ratio	% Thio-urea (Total Weight)	Roast Temp (°C) (60 min)	Cure Time (days)	% As Vola-tilized	TCLP Leachate Results		Distilled H_2O Leach 1st Extract			Distilled H_2O Leach 2nd Extract			Distilled H_2O Leach 3rd Extract			$NaHCO_3$ Leach 1st Extract			$NaHCO_3$ Leach 2nd Extract			$NaHCO_3$ Leach 3rd Extract			Uncon-fined Compres-sive Strength (psi)
						As mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	
0	-	---	---	---	---	2.36	6.2	5.18	11	7.9	4.47	12.8	7.7	6.22	9.8	8.6	26.7	36.6	8.4	105	119	10.7	115	182	10.9	---
1	3	---	---	5	---	7.91	11.5	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
1	3	---	---	28	---	8.81	11.8	9.24	13.1	12.4	60.7	11.6	12.4	5.38	29.4	12.4	12.8	25.0	12.9	89.1	12.8	12.5	11.7	23.9	12.4	5,220
2	3	---	600	5	7.7	0.05	11.6	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
2	3	---	600	28	7.7	0.32	11.8	0.03	1.51	12.4	0.03	7.36	12.4	0.04	26.7	12.6	0.44	6.4	12.9	48.4	5.99	12.5	13.2	17.1	12.4	5,350
3	1	---	---	5	---	37.9	11.4	---	---	---	---	---	—	---	---	---	---	---	---	---	---	---	---	---	---	---
3	1	---	---	28	---	30.1	11.5	40.7	40.1	12.3	15.5	19.7	12.3	17.0	29.7	11.8	35.9	47.3	12.8	24.6	23.4	12.4	40.2	26.1	12.3	5,000
4	1	---	600	5	6.2	0.22	11.4	---	---	---	---	---	---	---	---	—	---	---	---	---	---	---	---	---	---	---
4	1	---	600	28	6.2	0.28	11.5	0.27	1.87	12.3	0.16	4.52	12.3	0.20	9.98	12.3	1.02	8.16	12.8	15.9	5.13	12.5	30.2	12.7	12.3	5,570
5	0.5	---	---	28	---	51.9	11.2	82.4	76.5	11.9	23.9	31.2	12.2	15.1	21.0	12.1	106	93.5	12.2	49.9	35.8	12.1	70.6	26.3	11.9	3,670
6	0.5	---	700	28	5.9	1.0	11.2	0.20	3.26	11.9	0.04	6.14	12.1	0.07	12.3	12.1	0.66	3.62	12.2	6.04	2.43	12.1	38.7	4.79	12.0	2,890
7	0.2	---	---	28	---	74.2	8.9	101	98.8	11.6	15.7	25.9	11.9	7.18	31	11.8	127	122	11.6	130	52.8	11.8	83.6	29.1	10.0	---
8	0.2	---	700	28	32.5	34.8	9.1	0.51	2.66	11.5	0.41	3.15	11.7	0.51	3.46	11.8	1.33	1.16	11.7	65.4	1.65	11.5	82.4	3.92	10.5	---
9	1	1	---	28	---	39.2	11.7	49.4	122	12.1	12.4	31.7	12.3	9.17	18.8	12.4	70.9	124	12.2	14.7	31.7	12.2	24.7	17.6	12.1	3,730

* Uncast cement samples
--- Not analyzed or reagent not added

TABLE 5

ANALYTICAL RESULTS
CLAY PELLETIZED AND SINTERED SAMPLES

Clay Sample Ratio	Sinter Temp (°C) (15 min)	% As Volatilized	TCLP Leachate Results		Distilled H_2O Leach 1st Extract			Distilled H_2O Leach 2nd Extract			Distilled H_2O Leach 3rd Extract			$NaHCO_3$ Leach 1st Extract			$NaHCO_3$ Leach 2nd Extract			$NaHCO_3$ Leach 3rd Extract			Unconfined Compressive Strength (psi)
			As mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	As mg/L	TOC mg/L	pH	
VAULT																							
---	---	---	2,260	7.0	1,650	1,019	8.6	851	414	8.5	512	166	9.0	2,060	1,008	8.7	2,710	659	10.4	1,900	226	10.7	---
3	1,000	33	21.6	4.4	17.4	1.19	9.8	7.8	1.28	10.6	7.4	14.3	9.7	18.2	14.0	8.8	5.5	9.75	8.7	6.2	5.59	8.7	---
0.33	1,000	11	78.2	5.0	15.9	1.17	11.1	12.0	1.27	11.5	9.9	11.7	11.2	36.4	14.7	9.6	18.4	6.0	9.2	14.4	7.96	9.1	---
LAGOON SLUDGE																							
---	---	---	4.62	6.1	5.03	10	7.6	4.88	8.5	7.6	1.86	6.6	8.4	10.5	175	8.9	126	232	10.6	101	208	10.8	---
3	1,000	77	22.9	4.7	0.53	2.45	11.6	0.73	1.82	11.6	1.4	12.4	11.1	8.3	6.80	9.9	6.7	7.27	9.3	5.7	5.39	9.1	---
0.33	1,000	25	74.1	5.3	0.54	7.43	11.9	0.73	2.64	11.8	1.14	4.95	11.4	2.1	13.4	10.7	11.2	8.56	9.8	14.9	6.30	9.6	---
SLUDGE/SOIL MIXTURE																							
---	---	---	2.36	6.2	5.18	11	7.9	4.47	12.3	7.7	6.22	9.8	8.6	26.7	36.6	8.4	105	119	10.7	115	182	10.9	---
3	1,000	23.1	37.2	5.6	0.07	1.49	11.9	0.31	1.48	11.9	0.58	11.5	11.3	8.9	14.8	10.6	14.0	4.37	9.6	9.7	6.17	9.2	---
0.33	1,000	---	11.4	9.6	0.16	1.01	12.2	0.14	1.86	12.1	0.26	13.8	11.7	0.67	7.38	12.5	3.0	5.17	10.4	5.8	5.23	9.9	---

* Uncast cement samples
--- Not analyzed or reagent not added

EVALUATION OF THE SOLIDITECH SOLIDIFICATION/STABILIZATION TECHNOLOGY

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ABSTRACT

The Soliditech technology demonstration was conducted at the Imperial Oil Company/Champion Chemicals Superfund Site in Monmouth County, New Jersey. Contamination at this site includes PCB's, lead (with various other metals), and oil and grease.

The Soliditech process mixes the waste material with proprietary additives, pozzolanic materials, and water, in a batch mixer. Technical criteria used to evaluate its effectiveness include (1) short-term extraction and engineering tests, (2) long-term extraction and leaching tests, (3) petrographic examination, and (4) structural integrity observations.

Three different waste types--contaminated soil, waste filter cake material, and oily sludge--and a sand blank were treated. Fourteen cubic yards of treated waste monoliths, and nearly 300 cast cylindrical mold samples were produced.

Neither PCB's nor volatile organic compounds were detected in the TCLP extracts of treated wastes. Significantly reduced amounts of metals were detected in the TCLP, EP, BET, and ANS 16.1 extracts of treated wastes compared to untreated. Low concentrations of phenols and cresols were detected in post-treatment TCLP extracts. The pH of treated waste was near 12. Unconfined compressive strength of treated wastes was high; permeability was very low. Weight loss after wet/dry and freeze/thaw cycles was very low.

Portland cement contributed several metals to the treated waste. Physical stability of treated wastes was high. Data from all extraction and leaching tests showed negligible release of contaminants. Phenols and cresols appeared to be formed during the stabilization reactions.

INTRODUCTION

The EPA's Office of Research and Development has been carrying out the Agency's formal program to accelerate the development, demonstration, and use of new or innovative technologies which can provide permanent cleanup solutions for hazardous waste sites.

The Soliditech, Inc.'s waste solidification/stabilization process was the seventh technology to be demonstrated within this Superfund Innovative Technology Evaluation (SITE) program.

In cooperation with EPA's Office of Solid Waste and Emergency Response (OSWER), the Imperial Oil/Champion Chemical Superfund site in New Jersey was selected as the location to demonstrate the Soliditech SITE technology. This site is currently partially occupied by an active private company involved in blending and packaging oil products. Technical staff of the New Jersey Department of Environmental Protection (NJDEP) provided data describing the characteristics and extent of contamination at this site and assisted EPA in public relations aspects of the demonstration.

This technology demonstration was conducted in early December, 1988. A batch-mixer, a supply of portland cement, Urrichem(tm) reagent, other additives for their formulation, and accessory equipment were provided by Soliditech, Inc. The EPA's support contractor provided a sampling team. The demonstration was completed over a five-day period, resulting in nearly 14 cubic yards of solidified material, and over 300 individual samples for analyses of the numerous parameters applied to evaluate this technology.

PURPOSE

The primary goal of the SITE program is to evaluate the effectiveness of a technology by conducting a field-scale demonstration of each technology, collecting samples of treated waste materials and performing laboratory tests.

TEST METHODS

The Soliditech SITE technology evaluation was based on the results of laboratory tests on samples of waste material before and after treatment. Physical tests included ASTM procedures for particle size analysis, water content, and unconfined compressive strength (2); and TMSWC tests for water content, bulk density of treated waste, permeability of treated waste, and wet/dry and freeze/thaw tests on treated waste (3). Extraction tests included TCLP extraction, EP Toxicity, Batch Extraction Test, American Nuclear Society 16.1, and Waste Interface Leaching Test (1,4). EPA SW-846 methods were applied for pH, Eh, total dissolved solids, total organic carbon, oil and grease, volatile organic compounds, semivolatile organic compounds, polychlorinated biphenyls, and metals (6).

The Soliditech SITE Technology Demonstration was described in detail within the Demonstration Plan, which was written and peer-reviewed prior to initiation of field activities (5). This demonstration plan also included an approved Quality Assurance Project Plan, which described all planned sample acquisitions and analytical methods.

APPROACH

Contaminated soil was excavated from a pit approximately 5 feet wide, 3 feet deep, and 8 feet long in the designated "Off-Site Area One" of this Superfund site. Filter cake was collected from the open face of a waste pile (Figure 1). Oily sludge was scooped from an abandoned storage tank with a bucket, and stored in drums until the waste batch was processed. Approximately equal parts of oily sludge and filter cake were mixed to form the third waste type processed. All waste feedstock was screened to prevent large objects such as rocks, roots, bricks, or other debris from being incorporated into the treated waste. Although this debris would not have interfered with the Soliditech process, it was removed to prevent inclusion within samples taken for analytical testing.

Water was added to the waste within the mixer to provide the proper mixing consistency. Portland cement, other specific additives formulated by Soliditech staff, and Urrichem were then added and mixing was completed. The mixture was discharged from the mixer into one-cubic-yard plywood forms (Figure 1). Aliquots of the unsolidified mixture were taken from the forms and poured into 257 waxed cardboard and PVC cylindrical forms, of several different sizes, to provide material for the evaluation analyses (Table 1).

All of these materials were allowed to set for 28 days inside a heated warehouse; the cylindrical samples were then transported to the storage area of the analytical laboratory. The nearly 14 cubic yards of treated waste contained within the plywood forms to form the treated waste monoliths (TWM) were placed in a two-tiered stack and covered with a plastic sheet for subsequent long-term examination (Table 2).

Figure 2 shows the approaches that were used to evaluate the effectiveness of Soliditech's process. The Quality Assurance Project Plan, within the project's Demonstration Plan (5), specified the details of sample collection and preservation, analytical protocols, matrix and surrogate spike procedures, blanks, replicate analyses, and statistical procedures to be applied to data evaluation. Triplicate samples were provided for all analytical parameters in the treated material. The Demonstration Report (7) presents the complete data set resulting from this technology evaluation.

RESULTS

Table 3 shows the compositions of the waste treatment mixtures. The "Reagent Mixture" includes clean sand as a substitute for waste; the "Co-mixture" consists of approximately equal parts of filter-cake and oily sludge, because Soliditech preferred not to treat the oily sludge in its pure state.

Table 4 shows that, both before and after treatment by Soliditech, the density increased and water content decreased in all cases. The permeabilities of treated waste were very low; at values of 1 x 10-8 cm/sec and lower. The unconfined compressive strengths of the solidified wastes greatly exceeded those of the friable, and liquid in the case of the oily sludge, untreated materials.

Total chemical analyses of untreated and treated wastes showed a varying effect of dilution, depending upon the particular compounds of interest. PCB's varied from no observable change to over one-third less in the treated waste. Analyses of pure sand solidified using the Soliditech process showed that arsenic was present at 59 mg/Kg. Chromium, copper, lead, nickel, and zinc were noted to the extent of a few tens mg/Kg in this sand plus reagent mixture. A few mg/Kg phenols and cresols were detected in analyses of the treated wastes for semi-volatile organic compounds. The origin of these phenolics is uncertain, but laboratory contamination and contribution by the Soliditech additives and reagents have been ruled out. Volatile organic compounds were detected in levels up to nearly ten mg/Kg in the Off-site Area One soil and filter cake/Oily sludge mixture; except that 32 mg/Kg xylene was found in the latter. No volatiles were detected in analyses of the treated wastes; neither were any detected by monitoring the environment above the mixer as waste batches were being processed.

Table 5 shows the analytes found in TCLP extracts. Extracts of both untreated and treated wastes showed undetectable quantities of PCB's. Arsenic in the extract from treated Offsite Area One, at 0.020, and lead in the extract from treated Filter Cake, at 0.0020 mg/Kg were the highest levels of metals of concern detected. Chromium was found at 0.060 mg/L in extracts from both treated Filter Cake and treated sand reagent mix.

Analyses of EP extracts showed no detectable PCB's from either untreated or treated wastes. Table 6 shows the reductions in extractable contaminants after treatment.

The Batch Extraction Test (BET) includes crushing the sample to pass an ASTM No. 100 sieve (150 um), followed by 7-day extraction with distilled water of samples at the three solid-to-liquid ratios of 1:4, 1:20, and 1:100 (Cote, 1988). Data from this procedure provide an indication of the capacity of the sample (as a reservoir) to provide a source of leachable solutes. No PCB's were detected in any of these extracts. Aluminum, barium, calcium, and sodium were contributed by the portland cement added to the mixture; these were the major inorganics detected in the BET extracts. Lead was less than 0.05 mg/L (detection limit) in extracts at all three solid/liquid ratios; this immobilization occurred even where the untreated waste (co-mixture) released 1.7 mg/L into the 1:4 extract. Arsenic was present only at hundredth mg/L levels in all extracts of treated wastes, and decreased with decreasing solid/liquid ratio.

Data from ANS 16.1 leaching over 28 days show no detectable levels of PCB's, chromium, copper, lead, nickel, or zinc removed from any of the three treated wastes. Arsenic was present at 0.005 - 0.008 mg/L in all extracts from the treated Off-Site Area One waste. This represented the only presence of a contaminant of potential concern, and its concentration was quite low. A nearly constant quantity of Oil & Grease, between 1 - 3 mg/L, was removed during the 28-days of leaching. Thus, no contaminants of concern were removed in amounts sufficient to allow calculation of "Leachability Index," as prescribed by the ANSI/ANS-16.1-1986 procedure.

The Waste Interface Leaching Test (WILT) includes submersion of a monolithic material in distilled water, with drainage and analysis of solutes at two-week intervals. No PCB's could be detected in the WILT leachate from any of the treated wastes. Arsenic decreased by factors ranging from 20 to 100, to as low as 0.001 mg/L, among the three wastes treated, from the first to the sixth leaching increment. Lead was not detectable (<0.05 mg/L) in any of the leachates from treated wastes. Total dissolved solids decreased by about a factor of three from the first to the sixth leaching. Calcium, a good indicator solute derived from the portland cement, also decreased by about a factor of three from the first to the sixth leaching.

Petrographic examination of the solidified, treated wastes was planned in order to characterize the homogeneity of mixing, extent of curing of the concrete-like matrix, mineralogic composition of the solidified mass, voids within the solid matrix, and potential long-term weathering effects. In addition, morphologic examination of the treated waste monoliths (TWM) was planned to provide long-term data which describe how well these large blocks withstand environmental exposure. Preliminary observations show that the oil and grease appear widely dispersed in globules throughout both the cast cylinders prepared for laboratory study and the TWM's. Detailed characterization data will appear in a later report. Morphologic examination of the TWM's after 28-day initial curing showed a few large masses of oil and grease, suggesting that the first batch of waste processed in this technology demonstration may not have been thoroughly mixed. A few stress-relief cracks were noted along corners of a few of the TWM blocks.

CONCLUSIONS

The high unconfined compressive strength, very low permeability, and high resistance to wet/dry and freeze/thaw deterioration demonstrate a high degree of physical stability of the three treated wastes. Calculation of contaminant release from these solidified wastes by use of known diffusion coefficients can be expected to be accurate, since advective flow is so low.

Since the concentrations of all contaminants found in the EP and TCLP extracts of treated samples are so low, the Soliditech process has stabilized the contaminants of concern at the site of this demonstration. It is significant that as measured by TCLP, EP, BET, ANS 16.1, and WILT procedures, lead is barely detectable in extracts of treated wastes. This indicates a high degree of stability in a poorly leachable form within the treated wastes. The BET data confirm the stability of the treated wastes against leaching loss of lead and arsenic. The extremely low amounts of contaminant solutes found in the WILT leachates confirm the parallel findings in the shorter-term extraction tests--TCLP, EP, BET, and ANS 16.1.

Measurable amounts of arsenic, barium, chromium, copper, lead, nickel, and zinc appeared in the treated wastes. The source of these elements is believed to be portland cement. Decreases in loss-on-ignition are most likely due to dilution by the added cement.

The absence of any mechanical equipment problems during the demonstration illustrated the reliability of the Soliditech system. After the equipment operator gained familiarity with waste materials at this site, the process mixed all components into a homogeneous solidified product.

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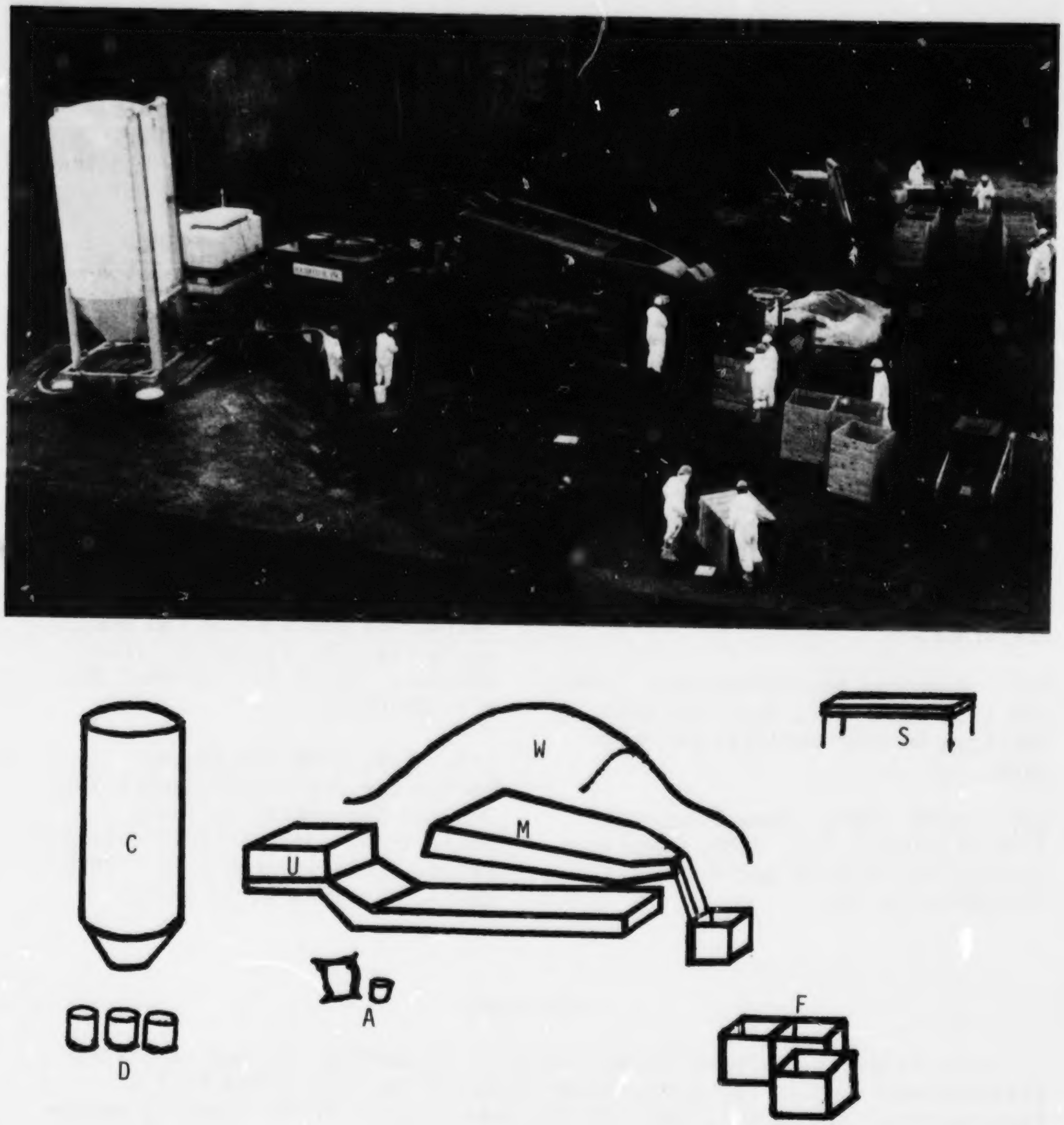


A - Proprietary additives
B - Portland cement supply
D - Drums containing oily sludge
F - Forms for treated waste monoliths

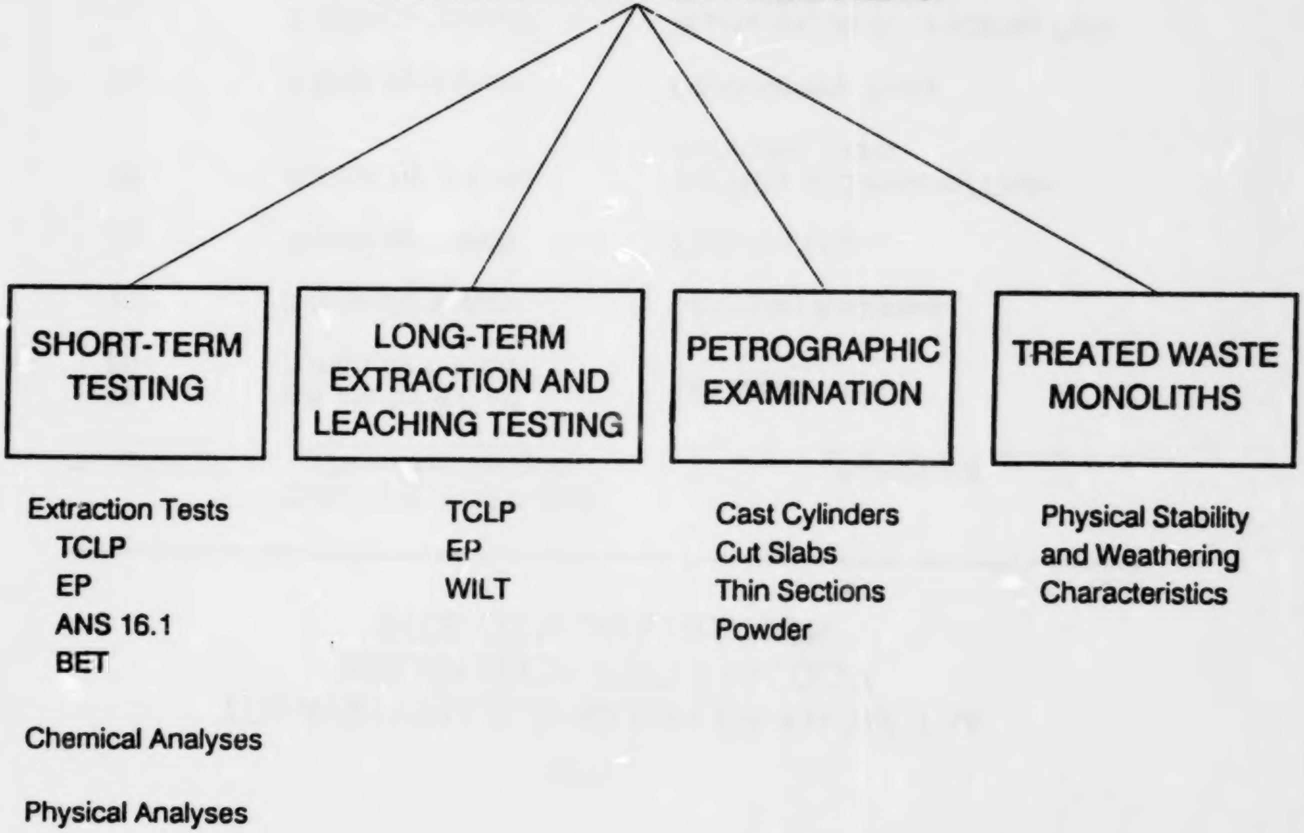
M - Mixer
S - Sample preparation
U - Urrichem supply
W - Filter cake waste pile

Figure 1. Soliditech Technology Demonstration Operations

FIGURE 2

SOLIDITECH TECHNOLOGY

EVALUATION PARAMETERS



SHORT-TERM TESTING

Extraction Tests
  TCLP
  EP
  ANS 16.1
  BET

Chemical Analyses

Physical Analyses

LONG-TERM EXTRACTION AND LEACHING TESTING

TCLP
EP
WILT

PETROGRAPHIC EXAMINATION

Cast Cylinders
Cut Slabs
Thin Sections
Powder

TREATED WASTE MONOLITHS

Physical Stability
and Weathering
Characteristics

TABLE 1

TREATED WASTE SAMPLES FROM THE SOLIDITECH TECHNOLOGY SITE DEMONSTRATION

QUANTITY	CAST CYLINDER SIZE (Diameter/Height)	PURPOSE
15 80	2.5 cm by 4.8 cm 3 inch by 6 inch	Extraction Tests
16	3 inch by 6 inch	Chemical Analyses
30	3 inch by 6 inch	Physical Tests
30	4.5 cm by 7.4 cm	Wet/Dry and Freeze/Thaw Durability Tests
12	3 inch by 3 inch	Permeability Tests
12 12	3 inch by 18 inch 6 inch by 18 inch	Waste Interface Leaching Test (6 months duration)
60	3 inch by 3 inch	Petrographic Tests

TABLE 2

TREATED WASTES FROM THE SOLIDITECH TECHNOLOGY SITE DEMONSTRATION

NUMBER OF BLOCKS	VOLUME AND WEIGHT	CONSTITUENTS
1	0.45 cubic yards 1,330 pounds	Clean sand plus Soliditech reagents and additives
3	3.08 cubic yards 9,110 pounds	Mixture of waste pile filter cake and oily sludge plus Soliditech reagents and additives
6	6.25 cubic yards 16,100 pounds	Waste pile filter cake plus Soliditech reagents and additives
4	4.10 cubic yards 11,700 pounds	Soil from offsite area plus Soliditech reagents and additives

TABLE 3. SOLIDITECH TREATMENT FORMULATIONS

	Reagent Mixture	Co-Mixture	Waste Pile	Off-Site Area
Waste Material (%)	56	40	59	58
Type II Cement (%)	31	51	16	29
Urrichem (%)	0.6	0.4	0.6	0.6
Additives (%)	1	1	0.9	0.9
Water	11	7	14	12
Total Weight (lbs)	1,420	9,760	19,100	15,700

TABLE 4. PHYSICAL PROPERTIES OF WASTE MATERIALS

	Filter Cake		Filter Cake/Oily Sludge Mixture		Off-Site Area One	
	Untreated	Treated	Untreated	Treated	Untreated	Treated
Bulk Density (g/cm^3)	1.14	1.43	1.19	1.68	1.26	1.59
Loss on ignition at SSOC (mg/Kg)	540,000	410,000	700,000	340,000	360,000	340,000
Permeability (cm/sec)	---	4.53×10^{-7}	---	8.93×10^{-9}	---	3.41×10^{-8}
Unconfined Compressive Strength (psi)	---	390	---	860	---	680
Water Content (%)	28.7	21.0	458.1	14.7	23.5	12.6

TABLE 5

MAJOR CONSTITUENTS DETECTED IN ANALYSES OF TCLP AND EP EXTRACTS

- Volatile Organic Compounds
  - Acetone
  - Benzene
  - 2-Butanone
  - Ethyl benzene
  - 4-Methyl-2-pentanone
  - Methylene chloride
  - Tetrachloroethene
  - Toluene
  - 1,1,1-Trichloroethane
  - Trichloroethene
  - Xylenes

- Semivolatile Organic Compounds
  - Benzyl alcohol
  - Butyl benzyl phthalate
  - o-Cresol
  - p-Cresol
  - 2,4-Dimethylphenol
  - bis (2-Ethylhexyl) phthalate
  - 2-Methylnaphthalene
  - Naphthalene
  - Phenol

- PCBs
  - Aroclor-1242
  - Aroclor-1260

- Metals (AA)
  - Arsenic
  - Lead
  - Mercury
  - Selenium
  - Thallium

- Metals (ICPES)
  - Aluminum
  - Barium
  - Beryllium
  - Cadmium
  - Calcium
  - Chromium
  - Copper
  - Lead
  - Nickel
  - Sodium
  - Zinc

- Other Chemical & Physical Tests
  - Eh
  - Filterable Residue (TDS)
  - Oil & grease, infared
  - pH

TABLE 6

CHEMICAL AND PHYSICAL ANALYSES OF EP EXTRACT FROM TREATED AND UNTREATED WASTE MATERIALS

	Filter Cake		Filter Cake/Oily Sludge Mixture		Off-Site Area One		
	Untreated	Treated	Untreated	Treated	Untreated	Treated	Reagent Mix
PCBs (μg/L)							
Aroclor-1242	<0.43	<0.41	<0.43	<0.42	<0.45	<0.21	<0.020
Aroclor-1260	<0.86	<0.82	<0.86	<0.84	<0.90	<0.42	<0.040
Metals (AA) (mg/L)							
Arsenic	0.010	0.0023	0.011	0.0020	0.18	0.028	<0.0020
Lead	0.26	0.0023	0.55	0.15	0.12	0.012	<0.0020
Mercury	<0.00020	<0.00020	<0.00020	<0.00020	<0.00020	<0.00030	<0.00020
Selenium	<0.0040	<0.0040	<0.0040	<0.0050	<0.0040	<0.0050	0.017
Thallium	<0.0010	<0.0010	0.0013	<0.0010	<0.0010	<0.0010	<0.0010
Metals (ICPES) (mg/L)							
Aluminum	<0.20	<0.20	<0.20	<0.20	0.40	0.20	0.50
Barium	0.21	1.4	1.1	5.7	0.58	2.4	4.3
Beryllium	<0.0020	<0.0020	<0.0020	<0.0020	<0.0020	<0.0020	<0.0020
Cadmium	<0.0050	<0.0050	0.0082	<0.0050	0.0052	<0.0050	<0.0050
Calcium	4.8	2,000	11	2,100	140	2,100	1,900
Chromium	<0.030	0.083	<0.030	0.037	<0.030	<0.030	0.067
Copper	<0.020	0.037	<0.020	<0.020	<0.020	0.060	<0.020
Lead	0.25	<0.050	0.52	<0.050	0.067	<0.050	<0.050
Nickel	<0.020	<0.020	<0.020	<0.020	<0.020	<0.020	<0.020
Sodium	1.4	15	58	45	2.1	16	35
Zinc	0.032	<0.020	0.86	<0.020	0.26	<0.020	<0.020
Other Chemical & Physical Tests							
Eh (mV)	320	-2.0	220	-30	130	-10	9.0
Filterable Residue (TDS) (mg/L)	90	9,500	330	9,100	790	9,400	8,700
Oil & Grease, infrared (mg/L)	<0.40	4.0	<0.40	3.1	2.6	11	<0.40
pH (pH units)	3.8	10.9	4.8	11.8	4.8	11.7	11.3

The Development of Screening Protocols
to Test
the Efficacy of Bioremediation Technologies

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ABSTRACT

The selection of technologies for the cleanup at National Priority List Sites often is made difficult with the diversity of proposed technologies and their relative abilities to treat the waste materials. Claims of treatment capability based on treatment of non-site materials may have no bearing on the treatment efficacy at a specified site. To profitably use the time period allotted to the evaluation of technology a more systematized approach is necessary. This can be accomplished is through the use of a defined bench scale evaluation of the candidate technology. Such evaluations should specify control conditions so that the results can provide an objective means of technology comparison and utility for the specified waste. Of the various technologies available for application to remediate hazardous waste sites, biological treatment is only now beginning to receive its deserved attention. Clearly, bioremedation is less developed, for this application, than some of the other technology options. In keeping with the general objectives of promoting the use of biological treatment and accomplishing quality cleanup objectives, this protocol development strives to provide a means to distinguish, at a small scale, promising biological treatment specifically targeted to the aerobic treatment of soil at a specific site. The protocol design permits the testing of a candidate biological treatment by a third party to provide an unbiased assessment of efficacy.

INTRODUCTION

The use of treatment technologies to achieve quality site cleanups has been emphasized as the only means to accomplish the intended goals of Superfund activities [1]. Biological degradation offers the potential for effective, safe, and inexpensive cleanup of hazardous waste contaminants at many Superfund sites. Biological treatment utilizes the various material cycles ie carbon, nitrogen and etc. to transform the toxic waste into benign products within the biosphere. Current biological technologies are based on the use of microorganisms native to a site or natural populations selected from sources apart from the site. The selection of native populations or organisms from other natural sources is made on the basis of compatibility with site conditions and/or the ability to degrade the organic pollutants at the site. Native organisms can be cultured in place through the addition of nutrients and growth supporting substrates.

Application of biological treatment to soils is in a development stage in terms of both biology and engineering. Simple effective inoculation with non native organisms to contaminated sites can be daunting. Novel bioreactor configurations (such as soil slurry reactors) are under study with very little performance data to support operation. In many cases optimal operation conditions are not known nor have these type of reactors received adequate attention even for proper performance estimates. In fact, current operations may be significantly distant from optimum conditions. The distinct possibility that abiotic processes(such as volatilization or sorption) significantly contribute to the overall "apparent" treatability of a biological process looms as a general unknown on the horizon[2,3,4]. Any evaluation of new and proposed treatment technology must be cognizant of the potential of abiotic processes to contribute significantly to the dispersal of pollutants. Abiotic transformations may not contribute to the intended conversion into non toxic products. The mere conversion of the contamination from one polluted phase to another, e.g. soil contamination volatilized to form air pollution, does not constitute a quality cleanup. From an economic viewpoint, it is important to design biological processes that treat the waste directly without relying on abiotic means for contaminant loss or dispersal.

Treatability claims based on treatment of waste materials other than those derived from the site slated for cleanup may give rise to treatment expectations that can never be realized at field scale. Other microflora, heavy metals and other environmental factors may negatively affect the ability of a biological treatment technology to meet its treatment goals. When non-native organisms are added to the site as part of the cleanup technology, there is the distinct possibility that predation by native organisms may occur. In one instance, physical separation and apparent loss of a complex pollutant from contaminated soil could have been misinterpreted as successful biological treatment[5]. The absence of a hazardous waste treatability data base for biological processes and the corresponding knowledge of operational conditions for these processes has prompted the development of this protocol [6].

PURPOSE

A performance protocol was devised for the testing of candidate biological soil treatment(s) proposed for hazardous waste site cleanup using site specific materials to determine on a small scale the efficacy of treatment based on the preceding considerations. This protocol is viewed as a means to distinguish between the relative merits of technologies competing as candidate technologies to accomplish site cleanup. The selection of optimal technology will assist the achievement of quality cleanups. This protocol is designed to narrow the field of competing cleanup biological technologies at the remedial investigation/ feasibility stage of site cleanup.

APPROACH

This paper presents the first of a series of protocols devoted to the formulation of an objective criterion to measure treatment. It is devoted to screening aerobic soil treatment technologies. The protocol is scheduled for use during the remedial investigation/ feasibility study(RI/FS) portion of the remedial process [7]. The data derived from the remedial investigation permits the targeting of technology to different portions of the site based on identity, quantity, and disposition of site contaminants. With selected biological technologies, it is possible screen for the most promising treatment using contaminated site materials.

The protocol provides the detailed, and tested set of instructions necessary for the evaluation of a biological treatment technology to determine the efficacy and suitability of a proposed treatment for a specific site using actual site materials. Essentially, the protocol is designed to assess the rate of transformation or treatment of contaminants through the analysis of contaminant concentrations and their changes with time. Short time periods are required for this analysis. The entire contents of the reactor flask are analyzed for each specified time frame in replicate numbers. The apparatus for this procedure is depicted in Figure 1. For each analytical time period specified in the rate analysis, a separate apparatus is required. For instance a rate study using an experimental plan of 3 periods in triplicate would require nine sets of experimental apparatus plus the control assemblies. The apparatus is designed to control and assess the effects of abiotic loss(eg. volatilization) and biotransformation.

All the appropriate best laboratory practices, sample handling instructions, appropriate experimental designs, and suitable quality assurance/quality control measures to provide a clear unequivocal estimate of treatment efficacy for a specific site are incorporated in the protocol. The new protocol uses information developed from field testing studies [8] and other protocols available in the literature [9,10,11].

Instructions leading to selection of samples and appropriate sampling techniques are presented. Directions for use of appropriate and necessary analytical chemistry measurements and their control are included. Reliance on existing and tested EPA analytical methodology was used to simplify the multitude of analytical options [12]. Design of the equipment assembly called for by the protocol is a reflection of the concern over control of avenues of abiotic loss attributable to volatilization, sorption, and photochemical conversions [13].

The protocol is designed to allow for general modifications recommended by the technology developer to permit the bench scale test to closely mimic large scale operating conditions. A reaction flask arrangement has been designated as the normal vessel containing the treatment Figure 1. A balanced gas trapping system is attached that permits the analysis for volatile losses completes the general assembly. The testing assemble is designed for ease of dismantling and the ability to wash down all surfaces that would potentially support deposition of waste substrates. Modifications of the simple flask configuration are permitted as long as the general objectives of manipulation and control of contaminant loss are maintained. Multiple assemblies are necessary for the conduction of the protocol since the flask contents are sacrificed to measure the extent of treatment. Replicate assemblies are necessary for each time period with the background control.

LIMITATIONS

This protocol has been designed to screen candidate biotechnologies designated for potential use for cleanup of a specific site. The data collected from this treatability testing provides a initial evaluation of rate and extent of conversion of site pollutants to detoxified products. The protocol has been designed to be economical. It therefore doesn't strive to completely define the rate of conversion since the scale of testing may not be totally comparable with full field scale operations. The testing assembly has been designed to insure control over all environmental loss pathways that may contribute to reduction of pollution concentrations. The use of mass balance is involved to ascertain that the loss of the hazardous waste chemical is the result of biodegradation and not some other abiotic process, such as chemical decay, volatilization, stripping or sorption, that may be encountered with full scale operations [13].

The data derived from these screening studies is not intended to predict the rate or extent of biodegradation at field scale [14]. The use of this data to predict costs of technology operational full scale or the time necessary for site closure is not supported by the design or intent of the designers of the protocol.

A new feature of this protocol is a section specifying the genotoxic testing of effluents from the treatment processes. Since the avowed direction of the technology is to detoxify contaminated materials, the protocol design team agreed that this is a desirable addition and may with time become a stand- along protocol. Current requirement for toxicity testing are those related to ecological testing and other tests such as the Ames test. It is quite possible that such toxicity testing may replace the current analytical requirements to assay the extent of treatment. Such a change is estimated to be less costly than the current analytical chemistry methodologies such as GC/MS. Until sufficient confidence can be placed in these new toxicity measurements, their effectiveness will be monitored by correlation with the results of GC or GC/MS studies.

DISCUSSION

Due to the diversity of treatment technology applied to a variety of contaminated environmental phases, a protocol for the evaluation of aerobic soil treatment technology was deemed to be the most desired by the site managers. A draft protocol has been peer reviewed and readjusted to correct points of deficiency. A testing phase is currently underway to determine the suitability of instructions given within the protocol. The results of this testing will be incorporated in the final version of the protocol. Protocols for the aerobic and anaerobic treatment of contaminated liquids are scheduled for future development. A protocol for the evaluation of anaerobic soil treatment technology will be developed in subsequent years.

ACKNOWLEDGMENTS

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

Table 1. Properties Assessed By Protocol

- Biodegradability of Contaminants
- Effectiveness of Nutritional Ammendments
  - Inorganic Supplements (N,P,S)
  - Electron Acceptors
  - Organic Growth Supplements
- Effectiveness of Innocula
  - Cultures of Native Organisms
  - Specific Degraders
- Abiotic Losses
  - Volatilization
  - Sorption
  - Leaching
- Genotoxicity of the Waste

FUNGAL BIOTRAP FOR RETRIEVAL OF HEAVY METALS FROM INDUSTRIAL WASTEWATERS

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ABSTRACT

Biotraps are living cells or specific cell components capable of removing or stabilizing toxic substances from waste streams. The fungus Penicillium ochro-chloron was discovered growing in an electroplating wastewater stream in Japan. It is not only tolerant to very high concentrations of divalent metal ions, but it can effectively remove heavy metals from almost any aqueous waste stream. P. ochro-chloron biotrap was prepared by growing spores in a glucose-minimal salts medium supplemented with 0.5 percent Tween 80 for 5 days with constant gentle agitation. The white mycelia beads 4-6 mm dia. were treated in a Buchner funnel with 80% ethanol to kill the cells, 15 percent sodium carbonate/bicarbonate pH 9.5, and then resuspended in an aqueous slurry at pH 4.0. The mycelia beads were used as an adsorbent in a batch experiment to determine copper-to-mycelia binding. The distribution coefficient K (concentration of copper ion in a solution/amount of copper bound to the mycelia) of 0.02 indicates this fungus should provide for efficient separations of copper by the mycelia in a continuous batch treatment system. Contercurrent distribution theory was employed to predict the behavior of a hypothetical copper waste stream passing through a continuous batch system employing the fungal biotrap as the immobile phase. This system should be capable of heavy metal uptake and recovery from both electroplating wastewaters and contaminated aqueous environments. The use of this fungus biotrap will rival synthetic cation exchange resins because of lower cost, lower weight per unit of exchange capacity and ease of application.

INTRODUCTION

Industries and government facilities which generate heavy metal wastes are now subject to a great deal of scrutiny by regulatory agencies, and they are also deluged with record keeping nightmares. Effluent streams from electroplating processes usually require chemical precipitation to remove contaminants before the water can be safely discharged into the environment. This in turn generates another form of hazardous waste, either a heavy metal sulfide or a heavy metal hydroxide sludge, which also must be disposed of according to strict regulations and these disposal practices are becoming more and more expensive (9). New processes developed through applications of biotechnology may allow industries to retrieve metals and to minimize disposal costs with corresponding economic and political benefits.

The resistance of many organisms to dissolved heavy metals (copper, cadmium, nickle, mercury, uranium, gold, silver for example) has been noted in bacteria, algae, water plants and some fungi (3-7). Most of the heavy metal resistant organisms have been derived from metal contaminated sites and by "enrichment selection".

PURPOSE

The purpose of this study was to evaluate one particular organism which was previously shown to survive and even reproduce in high concentrations of copper sulfate (4,5,8,10) as a potential biotrap for heavy metal retrieval and recovery from industrial wastewaters. The choice of organism for accomplishing the goal was Penicillium ochro-chloron (ATCC 42177) which was reported to be able to tolerate copper, zinc and manganese levels up to 100 g/L and cadmium to 20 g/L. Copper was also found to be accumulated by the organism up to 1 percent dry weight (3).

APPROACH

Fungus Cultures

P. ochro-chloron spores were harvested by suspension in deionized water from cultures growing in 15 cm Petrie dishes on corn meal agar (Scott Laboratories, Fiskeville, RI) after 4 days at 30°C. Spores are stored at 4° in deionized water. P. ochro-chloron mycelia grew in the form of dense spheres 3-6 mm diameter when spores were inoculated into 150 mL glucose minimal salts (GMS) medium (8) with 0.5% Tween 80 at 30°C, and swirled at 150 rpm in a rotatory shaker. These spheres or "beads" were then washed and treated with 80 percent ethanol for 30 min. Uptake of copper was enhanced if the ethanol-treated beads were then washed with a solution of 90 g. sodium carbonate and 60 g. sodium bicarbonate per L for 30 min. (pH 9.5) (7), and then exhaustively washed with distilled water adjusted to pH 4.0 with 1N HCl prior to use.

Cu-to-Mycelia Binding

A copper-to-mycelia binding experiment was then carried out. Two hundred mg of wet mycelia (approx 40 mg dry wt.) was placed into a 50 mL flask. Ten mL of a solution containing an appropriate concentration of copper sulfate at pH 4.0 was added and a 15 min. incubation was carried out swirling at 100 rpm at 25°. An aliquot of the solution was removed and assayed for copper by either atomic absorption or by colorimetric analysis using the bathocuproine method adjusted to a maximum sample size of 5 mL (1). Bound copper was determined from the difference between the initial amount of copper present and that found by assay. Copper uptake was optimal at pH values below 4.0 (10). Copper could be removed from mycelia with a wash in 1 percent HCl. The dry wt. of mycelia was then determined.

Electron Microprobe Analysis

In situ elemental analysis of fungal mycelia was carried out by electron microprobe analysis. Mycelia beads were dried, coated with a 100 A layer of carbon in a vacuum evaporator and subjected to energy dispersive X-ray microanalysis in a JEOL 300C Scanning-Transmission (STEM) electron microscope with a Kevex X-ray system.

PROBLEMS ENCOUNTERED

The greatest problem encountered was loss of heavy metal binding ability by the fungus when it was maintained on non-selective medium. It is recommended that cultures be maintained on 2000 mg/L Cu^{++}. Some brands of corn meal agar do not promote spore formation readily, but use of the Scott Laboratories product resulted in spore formation in only 5 days of incubation. Spores also lost viability if stored in phosphate buffered saline but not if stored in deionized water at 4°C.

RESULTS

Mycelia which were extensively washed with deionized water accumulate and retain copper as shown in the X-ray elemental microanalysis in Fig. 1. Lighter elements are also present in amounts which can be detected. In this analysis copper is present to about one percent dry wt of mycelia.

A titration experiment to determine binding parameters of copper (Cu^{++}) to *P. ochro-chloron* mycelia is shown in Fig. 2a. The ordinate represents the amount of copper bound (in micrograms) per mg dry wt. of mycelia. The abscissa represents the amount of free (unbound) copper in solution at equilibrium. The data are means of three independent determinations. The solid line represents the curve calculated from linear regression parameters shown in Fig. 2b. Here the data are represented as double reciprocal plots of values from Fig. 2a. The linear regression equation is given, with a correlation coefficient of 0.99 and $p<.001$. From the intercept with the ordinate the maximum binding of copper to mycelia was calculate to be 3.73 micrograms/mg.

The distribution coefficient K is defined as the amount of copper in solution (mg/L) in equilibrium with copper bound to mycelia (mg/Kg). This is analogous to a two phase system consisting of water and an immiscible solvent into which the solute can dissolve. In this situation the immiscible "solvent" is the mycelia. The data in Fig. 2 allow Kp to be determined at low values of copper in the linear portion of the curve. The value of Kp was found from this analysis to be 0.02.

Craig and Craig (2) showed that in a series of tubes each containing the same volume of two immiscible solvents a solute would partition according to K when the solute was first introduced into the first tube (tube 0). After equilibrium is achieved the upper solvent from tube 0 is transferred into the next tube (tube 1), new solvent is added to tube 0, and the tubes are shaken. At equilibrium the same type of transfer is again carried out with solvent being transferred from tube 1 to tube 2, from tube 0 to tube 1, and new solvent is added to tube 0. An expression was derived for the fraction of solute (Fn,r) in any tube after any number of transfers. K is the partition coefficient, n represents the number of the tube and r the number of the transfer:

$$F_{n,r} = [(n-1)!/r!(n-1-r)!] \times [K_{r+1}/(1+K)^n]$$

Although these relationships were derived for countercurrent distribution separation processes used by the pharmaceutical industry, they apply to the system described here as well. This is because fungal mycelia may be treated analogously to the lower immiscible solvent layer.

A simple computer program was written to enable the calculations of the fraction of solute in each tube in a series of 20 tubes after 19 transfers (Fig. 3) for various values of K. For values of $K<0.1$ the solute is retained in the lower solvent or in this case the mycelia of the first few tubes. In the case of P. ochrochloron beads serving as adsorbent for copper ion where $K = 0.02$ similar retention in a continuous batch process would be expected. The value of $K=10$ is also shown because this represents a probable value of K in the presence of 1 percent HCl. In this case the solute originally adsorbed to mycelia in the first few tubes would be expected to rapidly elute from the mycelia and could be collected in a small volume. Computer analysis for smaller numbers of tubes (5-11) using $K = .02$ shows similar results with the majority of the water soluble solute appearing in the upper solvent of the first tube.

A pilot plant or industrial continuous batch process might be expected to contain a more convenient number of tanks (represented by tubes in this analysis), perhaps less than 10. In addition, the ratio of liquid (wastewater) to mycelia in an actual process would not be 1:1 (an assumption made to derive the Craig equation) but more likely 10:1.

CONCLUSION

These studies are important in developing new methods for industrial wastewater treatment. The use of ehtanol-killed mycelia beads eliminates the need to immobilize cells or use heavy mats of fungal mycelia. The beads are easy to handle and process in column or batch systems. Heavy metal uptake occurs at sites within the cell wall matrix (5) and not within the cytoplasm. Uptake and release are achieved under conditions which are easy to manipulate. The fungus is a renewable product which should provide a cost-effective method for dealing with retrieval of heavy metals from contaminated wastewaters by continuous batch or column technologies.

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Disclaimer

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ENERGY DISPERSIVE X-RAY MICROANALYSIS OF P. *OCHRO-CHLORON* TREATED WITH $CuSO_4$

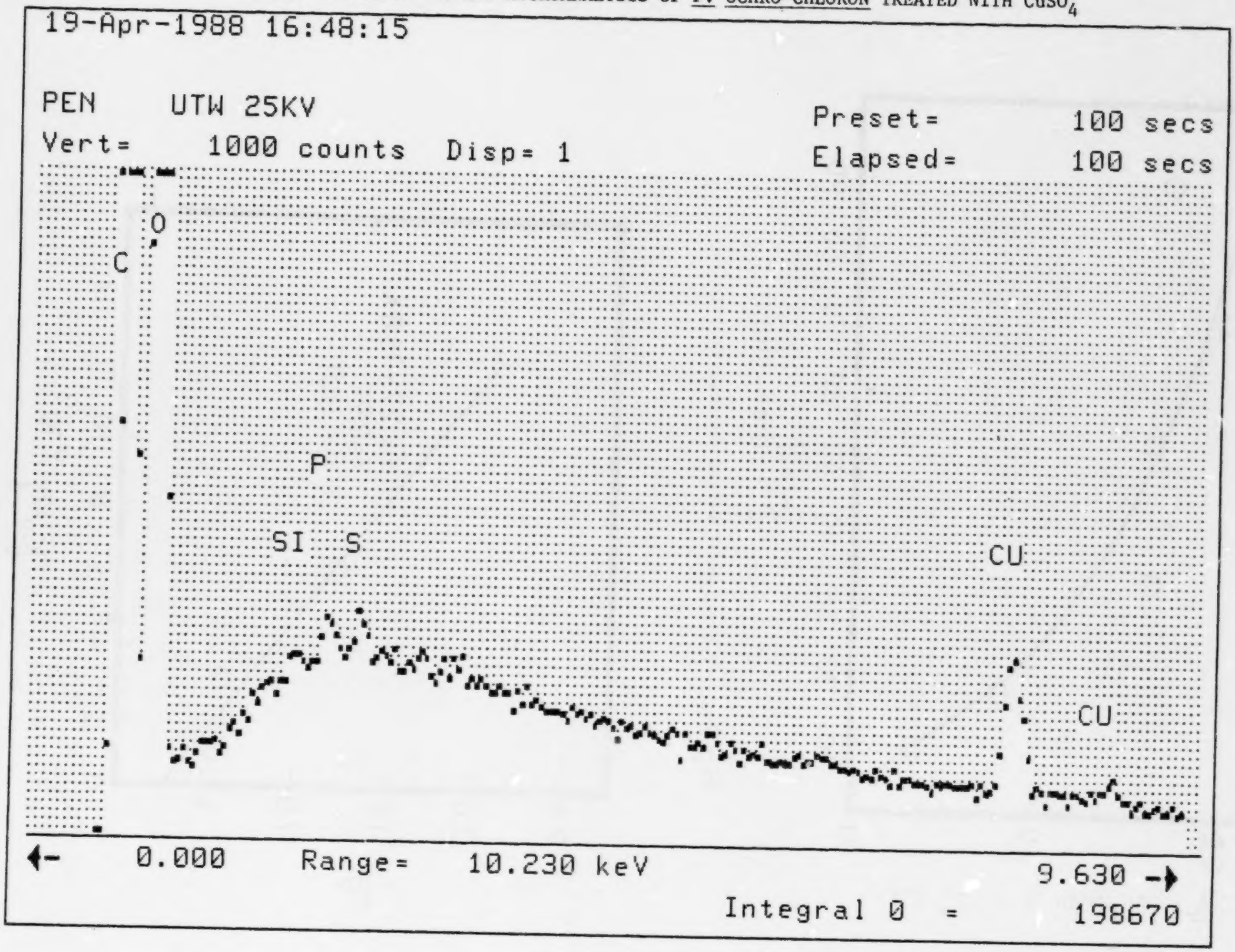

Fig. 1

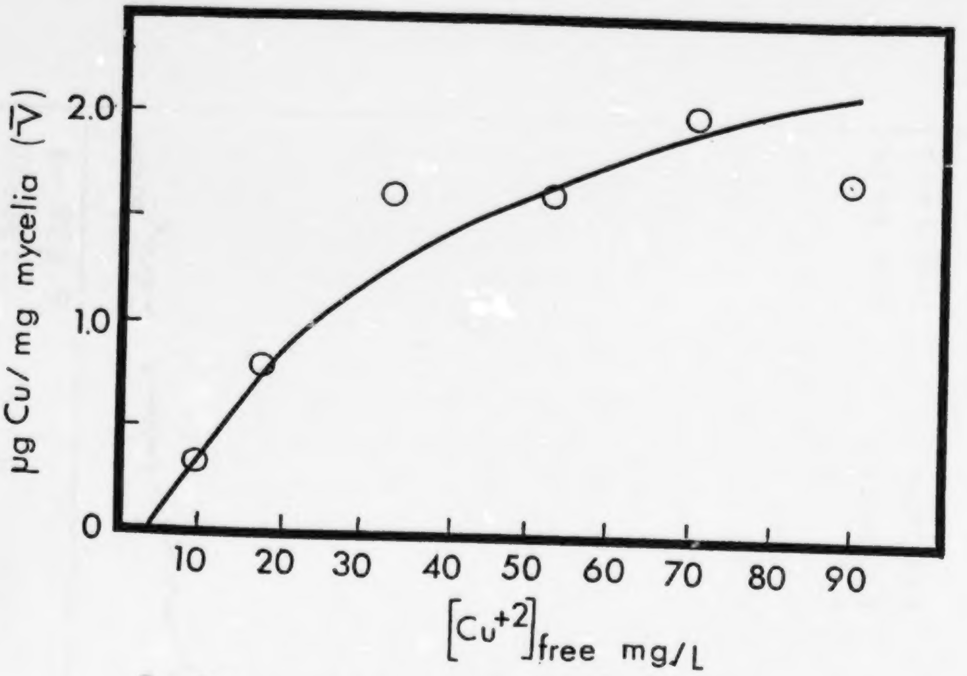

Fig. 2a. Titration of fungal mycelia with Cu^{+2}.

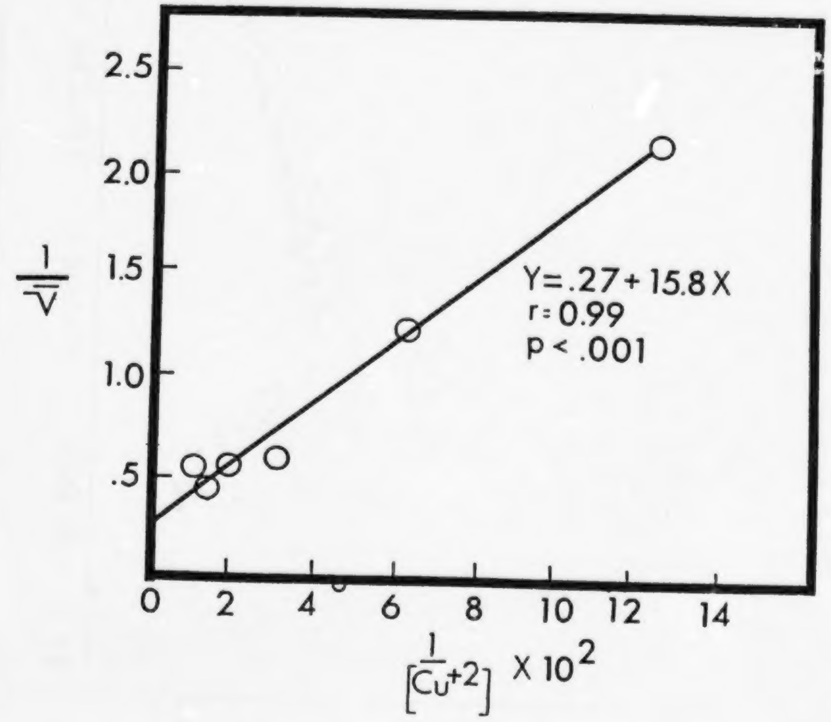

Fig. 2b. Double reciprocal plot of data from Fig. 2a.

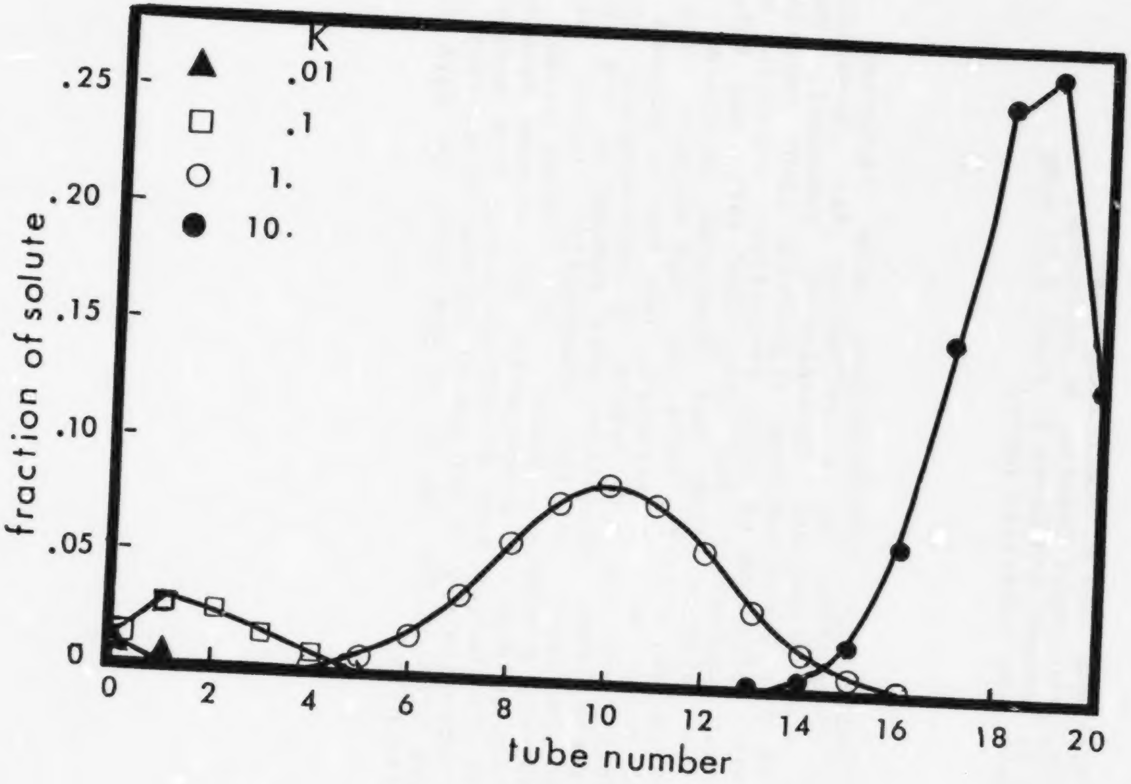

Fig. 3

Countercurrent distribution of a solute through 20 tubes for various values of K,

COMPOSTING OF EXPLOSIVES AND PROPELLANT CONTAMINATED SEDIMENTS

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Two field-scale demonstrations were conducted to investigate composting as a technology for remediating explosives and propellant contaminated sediments. Test sediments at the Louisiana Army Ammunition Plant contained approximately 76,000 ppm of total explosives, including TNT (66% of total explosive), RDX (25%), HMX (9%), and tetryl (0.3%). The mixture that was composted consisted of straw/horse manure, alfalfa, horse feed, and sediment. Two 12 cubic yard piles were constructed, one was maintained at approximately 35°C and the second at approximately 55°C. After 22 weeks, total explosives were reduced by 99% (from 17,872 to 74 ppm) in the thermophilic (55°C) pile. Transformation products peaked in concentration at approximately 20 days and subsequently fell to near detection limits. At the Badger Army Ammunition Plant, test sediments contained approximately 18,000 ppm of nitrocellulose (NC). NC was reduced from 13,086 ppm to 16 ppm after 101 days in a thermophilic pile.

Introduction

The manufacture and handling of explosives and propellants has resulted in soil and sediment contamination at U.S. Army munitions facilities, often as a result of previously acceptable waste disposal practices. The United States Army is currently investigating several technologies for decontaminating propellant- and explosives-contaminated soils. Among these candidate technologies is composting.

Composting is a process during which organic materials are biodegraded, resulting in the production of organic and/or inorganic transformation products and energy in the form of heat. This heat is trapped within the compost matrix, leading to the self-heating that is characteristic of composting. Composting for the purpose of hazardous substance destruction is initiated by mixing a matrix contaminated with biodegradable compounds (explosives and propellants in the present investigations) with organic carbon sources and bulking agents, which are added to enhance the porosity of the mixture to be composted.

Contaminants of concern at the Louisiana Army Ammunition Plant (LAAP) include 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro- 1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazocine (HMX) and N-methyl-N,2,4,6-tetranitroaniline (tetryl). Structural formulas for these compounds are presented in Figure 1. These explosives are found as contaminants in lagoon sediments as a result of the disposal of "pink water", which is generated from wash-down operations during munitions packing and loading. The name originates from the pink coloration the explosives produce in solution.

Previous research has indicated that TNT is microbially transformed, but is not completely mineralized to inorganic products [1,2,3]. Conditions that have been found to enhance the biotransformation of TNT include high organic carbon concentration and aerobic conditions [4]. Microbes generally catalyze nitro-group reduction of the TNT molecule [5]. A number of TNT biotransformation products are known. Evidence exists that these metabolic transformation products adsorb strongly to organic materials [6].

Anaerobic conditions and high organic carbon content have been found to enhance the biotransformation of RDX and HMX [4,7]. Laboratory-scale composting studies with ^{14}C-RDX have demonstrated high levels of $^{14}CO_2$ production (37 to 46 percent of initial ^{14}C activity added), suggesting ring cleavage and complete mineralization [8].

The contaminant of concern at the Badger Army Ammunition Plant (BAAP) was nitrocellulose (NC). NC may contain from 11.1 percent nitrogen (cellulose dinitrate) to 14.5 percent nitrogen (cellulose trinitrate). NC has been found to be susceptible to microbial attack in lab and pilot-scale composting systems [8].

The primary objective of these studies [9, BAAP report in preparation] was to evaluate the utility of aerated static pile composting as a technology for remediating soils and sediments contaminated with the explosives TNT, HMX, RDX, and tetryl and the propellant nitrocellulose. Secondary objectives included evaluating different materials handling and process control strategies and determining transformation products when Standard Analytical Reference Materials (SARMs) were available.

Materials and Methods

Two 8-inch-thick concrete test pads were constructed 20 feet apart adjacent to the pink water lagoons at LAAP. Drainage channels in the pads were connected to a sump located below grade. Water from the sump was reapplied to the compost piles.

The mixture to be composted at LAAP was prepared using horse manure and soiled bedding (straw), alfalfa, horse feed (Purina Balanced Blend 14), and contaminated sediment. Sawdust, wood chips, and baled straw were used to construct bases and insulating covers (see Figure 2).

A mechanical feed system, developed initially to meter explosives-contaminated soil into an incinerator, was used to homogenize sediment and to mix the material to be composted.

Dual-channel strip-chart recorders (Omega Engineering) were used to continuously record compost temperatures. Two landfill thermocouple probes (Atkins Technical) were placed in each pile. One probe was placed 2 feet inside each pile, 3 feet above pad level, and 2 feet from the blower end of the pile. The other probes were inserted into the center of each pile. A landfill probe equipped with a hand held digital thermometer was used to monitor temperatures daily at 6 locations in each pile.

Each compost pile contained a system of perforated and nonperforated polyethylene drainage tubing (ADS, 4-inch diameter) placed on top of a wood chip base and connected to an explosion-proof radial-blade blower. The blowers were used to pull air through the compost piles. Blower cycling was controlled by both timer and temperature feedback systems. The temperature feedback system consisted of soil thermistors that measured compost temperature and panel-mounted Fenwal series 551 thermistor sensing temperature controllers.

The mixture to be composted was prepared as follows. Sediment (excavated and homogenized 2 weeks previously and analyzed for explosives concentration) was reprocessed through the feed system once. Horse feed was mixed into the sediment on the mixing pad using an excavator bucket. Straw/manure, alfalfa, and 35 pounds of fertilizer (13-13-13) containing nitrogen (13 percent w/w), phosphorous (5.7 percent w/w), and potassium (10.87 percent w/w) were added to the mixture. The materials were mixed using an excavator and front-end loaders for 30 minutes. The mixture was processed through the feed system once. Each load of compost was moistened with water as it was delivered to the pads. Approximately 400 gallons of water were applied to each compost pile. Table 1 shows the amount of each material in the mixture.

Pile construction was completed and the temperature control systems and recorders started on 25 February 1988. Samples were analyzed for contaminant concentration nine times over a 153-day test period. The compost piles were individually dismantled, remixed, and remoistened at day 33, 60, and 111.

Analyses for lead, selenium, and arsenic were conducted by procedures in Standard Methods for Chemical Analysis of Water and Wastes (U.S. EPA 600/4-79-020, 1979). Compost samples were analyzed for TNT, RDX, HMX, tetryl, and transformation products by USATHAMA Method LW02, modified for the extraction and analysis of compost. Compost samples were analyzed for NC by USATHAMA Method LY02.

The BAAP field demonstration was similar to the LAAP demonstration except that cow manure was used instead of horse manure/straw, an agricultural mixer (Knight Manufacturing) was used to prepare the mixture, and 6 thermocouple probes were used in each pile. Table 2 shows the amount of each material used in one of the four piles constructed at BAAP.

Results

The LAAP sediment contained TNT (56,800 mg/kg), RDX (17,900 mg/kg), HMX (2,390 mg/kg), and tetryl (650 mg/kg). The sediment was combined with the other components of the mixture to be composted according to the materials balance presented in Table 1.

The BAAP sediment for piles 1 and 2 contained 18,800 ppm of NC, and for piles 3 and 4, 17,027 ppm of NC. The sediment was combined with the other components of the mixture to be composted in pile 3 according to the materials balance presented in Table 2. Piles 1 and 2 contained 3 percent soil by weight. Pile 3 contained 22 weight percent soil and pile 4 contained 32.5 weight percent.

Total explosives (summation of TNT, RDX, HMX, and tetryl) concentrations in piles 3 and 4 at the beginning of the study were 16,460 and 17,870 mg/kg, respectively. After 153 days, the concentration of total solvent extractable explosives in pile 4 was 74 mg/kg. A linear plot of total explosives concentration versus time for the thermophilic pile is presented in Figure 3. The mean and standard deviation at each time point represents at least three and as many as nine replicate samples.

Samples of water from the sump were analyzed for explosives and transformation products on days 0, 16, 22, and 153. The analytes were below detection limits, which varied depending upon the age of the sump water, in all sump water samples tested.

Day zero compost samples were analyzed for TNT transformation products. Concentrations of transformation products peaked in concentration at approximately 20 days and subsequently fell to near detection limits.

The physical appearance of the compost changed considerably over the 153-day test period. When the compost was initially mixed, it had a highly fibrous appearance, a rough texture, and it smelled conspicuously of the manure, urine, and feed used to prepare it. After approximately 100 days, the compost had become more soil-like and less fibrous in appearance. At the end of the test period, the compost had both the appearance and smell of loamy soil.

NC in pile 2 (thermophilic) at BAAP was reduced from 3,039 ppm at day zero to 59 ppm at day 70. A linear plot of NC concentration versus time for pile 2 is presented in Figure 4. The NC concentration did not change significantly over the remainder of the 153 day test period.

The variation in NC concentration for any given sampling time (representing 5 individual samples) decreased with time. Duplicate analyses for any one sample showed good reproducibility. However, at earlier stages of the test period, significant differences were observed in NC content between different sampling locations within all four piles studied at BAAP.

Discussion

The concentration of solvent-extractable total explosives was significantly reduced during the 153-day LAAP test period. Fate mechanisms that may have been responsible for contaminant reduction include sorption of explosives and transformation products to the compost matrix, incorporation of explosives and transformation products into environmentally stable molecules, and mineralization of explosives to carbon dioxide, water, and other inorganics.

Previously published literature indicates that biotransformation of TNT, RDX, and HMX does occur. However, with the exception of RDX [8], significant mineralization of these compounds has not been demonstrated. Work by Kaplan and Kaplan [6] indicated that incorporation of chemically reactive transformation products into compost matrices increased with increasing compost age and was the primary fate process involved in explosives composting. These studies were, however, conducted at laboratory scale in externally heated flasks. Consequently, microbial community development and the corresponding metabolic activity may have been less than that observed in a large scale compost. The significance of mineralization in the present study cannot be determined from the data generated.

Previous research on explosives composting with ^{14}C-labeled test materials has demonstrated extensive (and apparently nonreversible) binding of ^{14}C activity to a compost matrix over time [3,8]. In one study [8], less than 1 percent of the initial ^{14}C activity (spiked as ^{14}C-TNT into compost) was recovered as $^{14}CO_2$ after 6 weeks of composting, while 66 percent of the ^{14}C activity became bound to the compost matrix and was unextractable. The production of organic transformation products from TNT, RDX, and HMX is well documented [10,11]. In the present study, TNT transformation products were detected in initial compost samples, increased in concentration over the first several weeks of the test period, and decreased to low mg/kg levels thereafter. These data do not support one environmental fate process over another.

The concentration of solvent-extractable NC was significantly reduced during the 151-day test period for piles 1 and 2 at BAAP. The same fate processes potentially responsible for the loss of explosives at LAAP also could be responsible for NC loss at BAAP. Previously published literature [8] indicates that mineralization of NC does occur. Therefore, it is probable that NC was mineralized to some extent during the BAAP field demonstration. However, the exact contribution of mineralization by microbial activity cannot be determined from the data collected.

The results of these field demonstrations indicate that composting is a feasible technology for reducing the extractable concentrations of NC and explosives/transformation products in contaminated soils and sediments. Consequently, composting may be a suitable technology for remediating propellant- and explosives-contaminated soil and sediment. The compost residue, however, must be acceptable for disposal in a manner which makes composting cost effective. Additional chemical characterization of the residue as well as residue toxicity studies are recommended.

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Disclaimer

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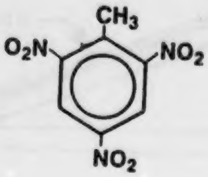
Table 1.
Materials balance of mixture to be composted at LAAP.

Material	Volume (cu yd)	Mass (lb)	Percent	
			Volume	Mass
Sediment	1	2,300	3	24
Alfalfa	13	940	38	10
Straw/manure	16	2,480	47	25
Horse Feed	4	4,000	12	41
Total	34	9,720	100	100

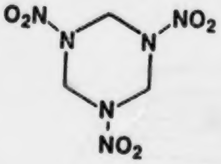
Table 2.
Materials balance of mixture to be composted in Pile 3 at BAAP.

Material	Volume (yd³)	Mass (lb)	Percent	
			Volume	Mass
Soil	1.50	2,550	11.8	22.2
Alfalfa	5.2	904	40.9	7.9
Feed	1.6	1,776	12.6	15.5
Woodchips	0.7	440	5.5	3.8
Manure	3.7	5,800	29.1	50.6
Total	12.7	11,470	100.0	100.0



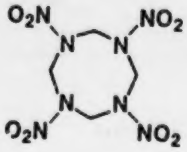
2,4,6-Trinitrotoluene

TNT



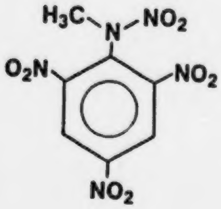
Hexahydro-1,3,5-Trinitro-1,3,5-Triazine

RDX



Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetraazocine

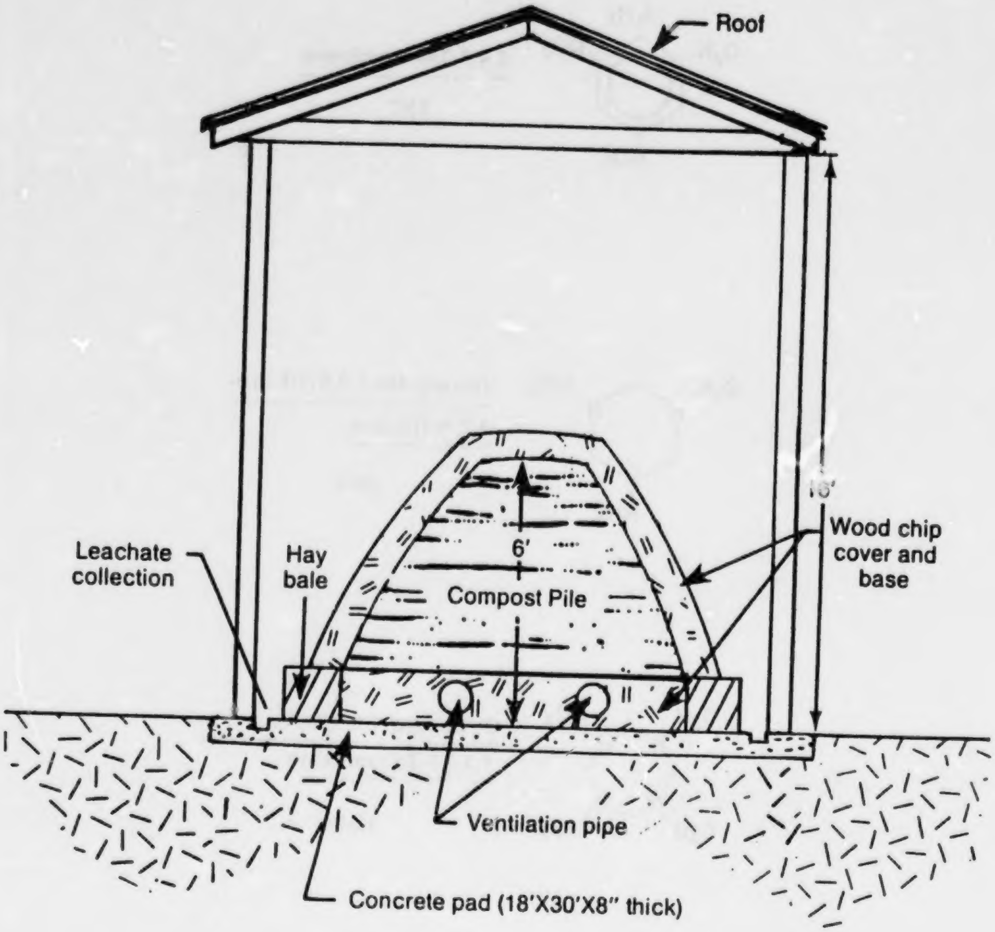
HMX



N-Methyl-N,2,4,6-tetranitroaniline

Tetryl

Figure 1. Structures of explosives of concern at LAAP.


Roof
16'
Wood chip cover and base
Leachate collection
Hay bale
6'
Compost Pile
Ventilation pipe
Concrete pad (18'X30'X8" thick)

Note: Schematic only, not to scale.

Figure 2. Cross-section schematic of compost pile with roof, Louisiana Army Ammunition Plant.

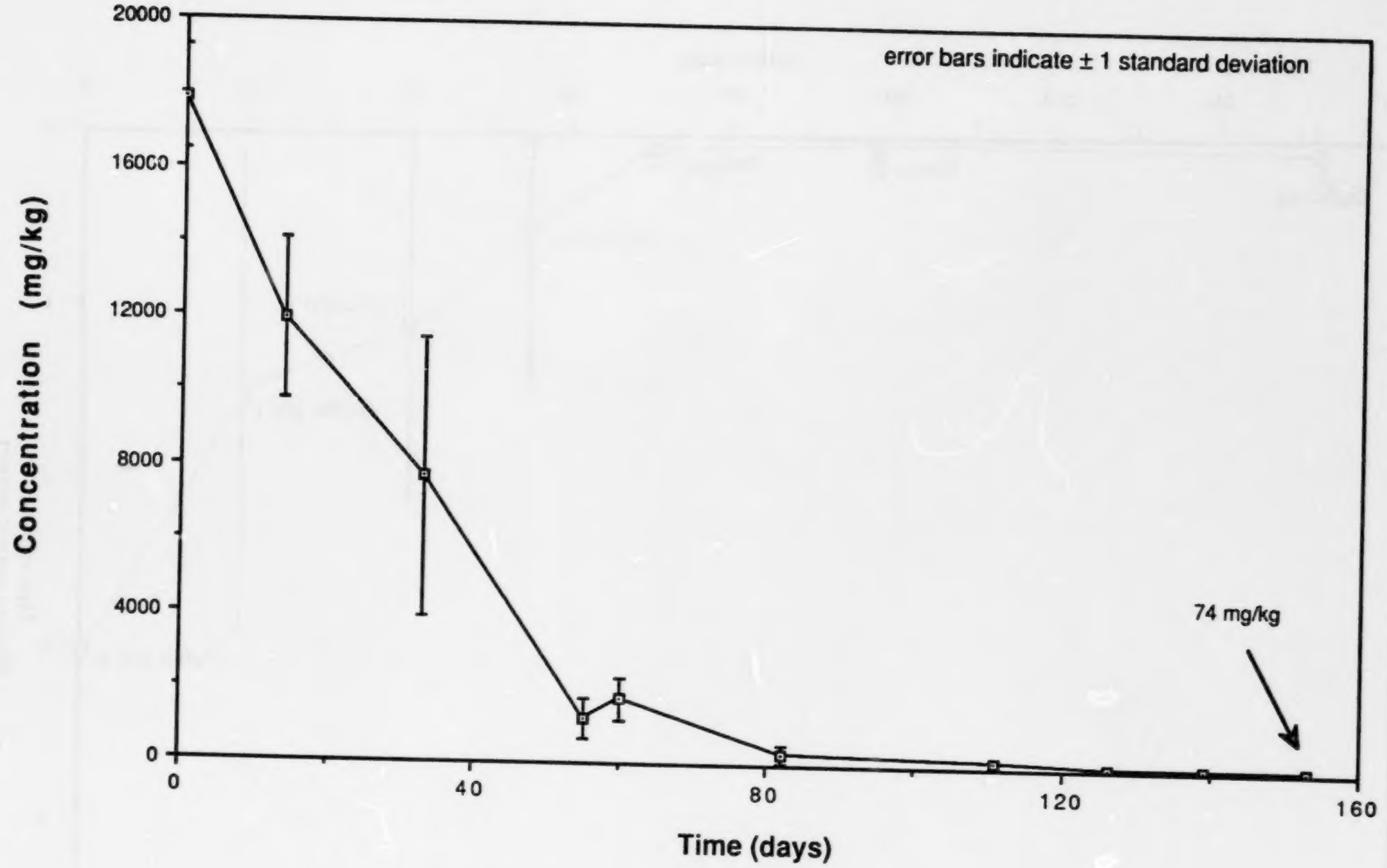


Figure 3. Concentration of Total Explosives in Thermophilic Compost Pile at LAAP

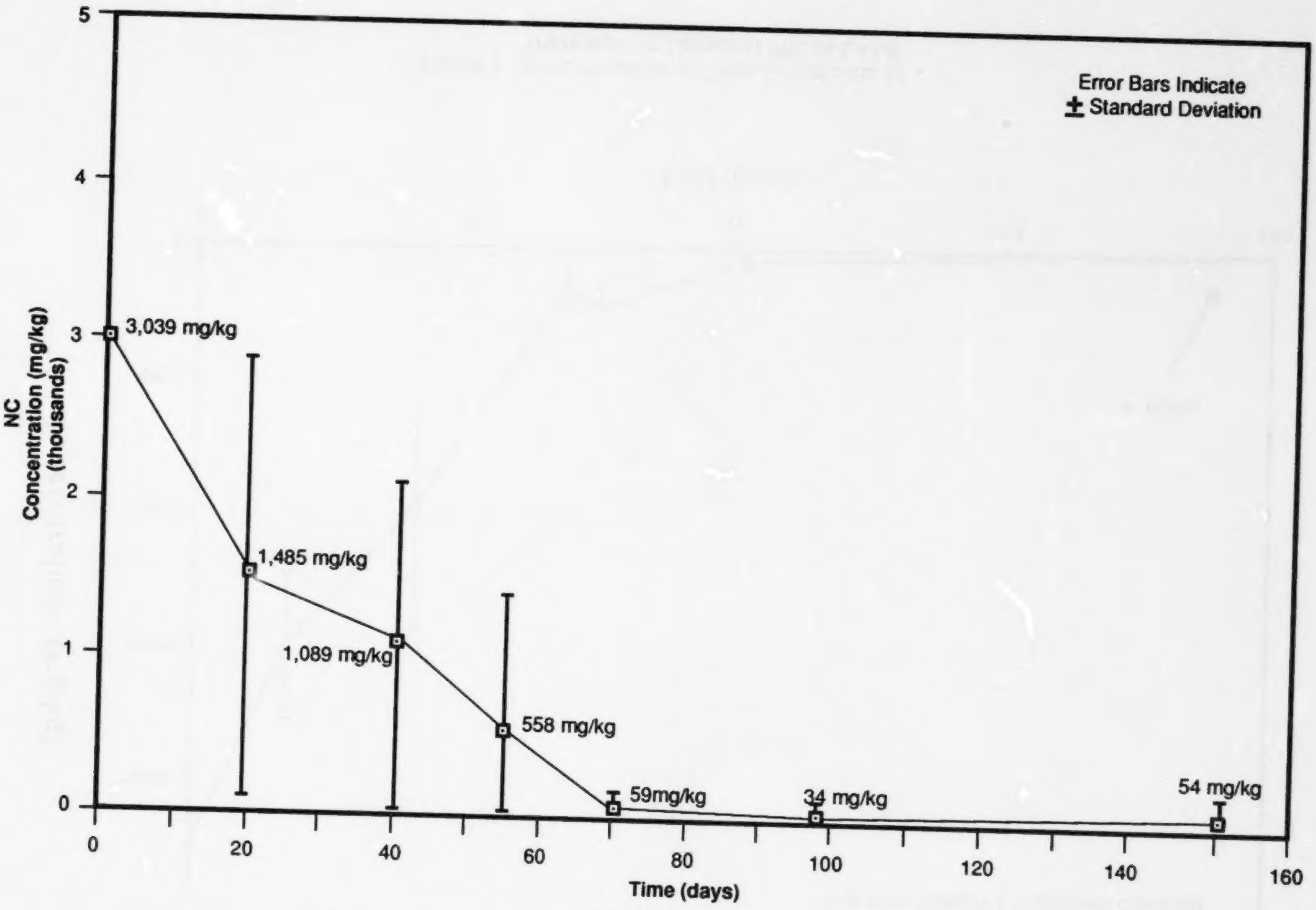


Figure 4. Concentration of nitrocellulose in Thermophilic Compost Pile at BAAP.

A NEW BIOTECHNOLOGY FOR RECOVERING HEAVY METAL IONS FROM WASTEWATER

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ABSTRACT

Bio-recovery Systems has developed a new sorption process for removing toxic metal ions from water. This process is based upon the natural, very strong affinity for biological materials, such as the cell walls of plants and microorganisms, for heavy metal ions. Biological materials, primarily algae, have been immobilized in a polymer to produce a "biological" ion exchange resin, AlgaSORB®. The material has a remarkable affinity for heavy metal ions and is capable of concentrating these ions by a factor of many thousand-fold. Additionally, the bound metals can be stripped and recovered from the algal material in a manner similar to conventional resins.

INTRODUCTION

Bio-recovery Systems has developed a new sorption process for removing toxic metal ions from water. This process is based upon the natural, very strong affinity of biological materials, such as the cell walls of plants and microorganisms, for heavy metal ions. Biological materials, primarily algae, have been immobilized in a polymer to produce a "biological" ion exchange resin, AlgaSORB®. The material has a remarkable affinity for heavy metal ions and is capable of concentrating these ions by a factor of many thousand-fold. Additionally, the bound metals can be stripped and recovered from the algal material in a manner similar to conventional resins.

PURPOSE

This new technology has been demonstrated to be an extremely effective method for removing toxic metals from groundwaters. Metal concentrations can be produced to very low parts per billion (ppb) levels. An important characteristic of the binding material is that high concentrations of very common ions such as calcium, magnesium, sodium, potassium, chloride and sulfate do not interfere with the binding of heavy metals. Waters containing a total dissolved solids (TDS) content of several thousand and a hardness of several hundred parts per million (ppm) can be successfully treated to remove and recover heavy metals. The process is particularly effective in removing mercury, lead and cadmium, but also works well for other metals such as chromium, copper, nickel, zinc, uranium, cobalt and manganese.

Past waste disposal practices have caused serious heavy metal contamination to many groundwater supplies. Both acute and chronic illnesses in humans, animals and plants can be caused by even very low concentrations of heavy metals. A major source of these contaminants is leachates from legal and illegal landfills and drainages from old mines. This problem is increasing, and attention is being focused on the development of new methods to remove heavy metals from groundwater.

Scientists at Bio-recovery Systems have developed a proprietary sorption technique for removing heavy metals from contaminated wastewaters. This process is based upon a very strong affinity of heavy metal ions for functional groups on algae cells. The algae cells are non-living and have been immobilized in a silica polymer to produce a "biological" ion exchange resin called AlgaSORB®. Figure 1 shows the reaction of divalent and trivalent metal ions with an algal cell. The metal ions interact with various chemical groups on the cell surface to produce a very strong complex.[1]

AlgaSORB® functions as a biological ion-exchange resin. Like ion exchange resins AlgaSORB® can be recycled. Metal ions have been sorbed and stripped for as many as 75 cycles over a two-year period with no noticeable loss in efficiency. AlgaSORB® is superior to synthetic ion exchange resins when the wastewater being treated is high in total dissolved solids or organic materials. Under these conditions synthetic resins would be either inefficient or would be unoperational. Thus, AlgaSORB® is particularly efficient in removing heavy metals from groundwaters which naturally contain high TDS.

Over the past two years Bio-recovery Systems has been awarded two Small Business Innovative Research (SBIR) contracts and a contract as part of the Emerging Technologies program under the auspices of the Superfund Innovative Technologies Evaluation (SITE) program. All three of these contracts were from the United States Environmental Protection Agency to research and develop the AlgaSORB® technology for commercial applications. Results from these contracts, some of which are summarized below, clearly show the efficiency of AlgaSORB® for removing heavy metals from a variety of sources and have led to commercialization of the technology.

APPROACH

The testing of metal ion binding by algae was performed in a column configuration. These experiments were performed by passing the metal-containing solutions through a column that was packed with AlgaSORB®. Metal ion analyses were preformed on both the influent and effluents from the column, and the metal binding was determined from the difference in the metal concentration in influent and effluent fractions. Effluents were often collected from these columns until "breakthrough" of metal occurred, and often sufficient volumes of metal-containing solutions were passed through the columns until the effluent concentrations of metal ion was the same as influent concentration. At that point the column was washed with deionized water and a stripping solution was passed over the column. Effluents containing stripped metal ions were then analyzed for metal content.

All experiments were performed in duplicate or triplicate to insure that results were reproducible. Careful attention was given to the control of pH, and cell-free control experiments were performed to insure that no precipitation of metal ions (such as metal hydroxides) occurred as a result of pH adjustments or the addition of other ions.

The techniques used for metal ion analyses included atomic adsorption spectrophotometry, graphite furnace analysis, direct current argon plasma spectrophotometry, and/or ultraviolet-visible spectrophotometry. Solutions and standards were matrix matched, or the method of standard additions was used wherever necessary. Complete details of metal ion analyses are found in recent publications.[1-6]

RESULTS

Removal of Heavy Metals from Groundwater

A. Removal of Copper from Contaminated Groundwaters Containing Halogenated Hydrocarbons. Bio-recovery Systems obtained groundwaters which had been contaminated with copper, tetrachloroethylene and dichloroethylene by a printed circuit board manufacturer. These waters contained a total dissolved solid content (TDS) of nearly 2000 ppm and had a total calcium and magnesium content of approximately 300 ppm. Past experience had shown that ion exchange resins were not effective in treating these waters for copper removal because of i) the high mineral content and ii) the propensity of the resins to become clogged with the organics in these waters. However, experiments showed that 400-bed volumes of the copper containing waters could be passed through a column (0.7 cm ID x 13 cm high) containing AlgaSORB® without effluents from the column containing more than 0.01 ppm of copper. The experiments were stopped at 400-bed volumes, so undoubtedly larger volumes of waters could have been treated before unacceptable levels of copper appeared in the effluents.

After 400-bed volumes had been passed through the AlgaSORB® column, the bound copper was, within experimental error, completely stripped from the column by the passage of 0.5M H_2SO_4 through the column. Again, as with the cadmium stripping, the copper was almost completely stripped within the first few bed volumes.

B. Removal of Cadmium from Waters at a Superfund Site. Officials from U.S. EPA Region II arranged to supply samples from a well at a Superfund site in New Jersey, the Waldick Aerospace Devices site. These waters contained, among other things, cadmium at a level of 0.13 mg/L. The waters, at a pH of 6.0-7.1, also contained 0.66 mg/L of a halogenated hydrocarbon, tetrachloroethylene as well as other organics. Organics, of course, are well known to interfere with the function of traditional ion exchange resins.

A column containing AlgaSORB® (0.7 cm ID x 13 cm high) was prepared, and the Waldick Aerospace waters were passed through the column. Five milliliter fractions of water exiting the column were collected until 500 mL (100-bed volumes) of Waldick waters were passed through the column at a flow rate of one-sixth of a bed volume per minute (total bed volume was 5.0 mL). Each fraction of effluent was analyzed for cadmium using graphite furnace atomic absorption spectrometry. All effluent fractions showed that cadmium concentration was near or below 0.001 mg/L through the passage of the 100-bed volumes of the cadmium-containing solution. Because the experiment was stopped after the passage of 100-bed volumes through the column, it is not possible to state explicitly what volume of solution could be treated before cadmium breakthrough occurred. However, experience has shown that if a test material is capable of treating at least 100-bed volumes, it will be economically feasible to use the material. The essential point is that the AlgaSORB® removed cadmium well below those levels which are allowed in drinking water. The current drinking water levels for cadmium stand at 0.005 mg/L.

Once 100-bed volumes of the cadmium-containing solution had passed through the AlgaSORB®-containing column, cadmium was stripped from the column by passing 0.15M H_2SO_4 through the column. Analysis of the column effluents showed that nearly 90 percent of the cadmium was stripped from the column with the passage of two-bed volumes of sulfuric acid through the column. Most of the remainder of the cadmium appeared in the next two-bed volumes. Mass balance calculations showed that, within experimental error, all of the bound-cadmium was stripped from the column. Once the cadmium was stripped from the column, the column was ready for reuse after rinsing with distilled water. Subsequent passage of cadmium-containing water through the column showed similar cadmium binding properties.

C. Removal of Nickel and Chromium from Contaminated Groundwater. A sample of groundwater that had been contaminated with nickel and chromium was obtained directly from the electroplating business which was responsible for the contamination. Presently the electroplater is pumping and treating these groundwaters with a conventional (precipitation) wastewater treatment system. The initial pH of the groundwaters was near pH 7. The chromium content (essentially all hexavalent chromium) was near 0.9 mg/L and nickel content was at 2.7 mg/L. The customer's discharge levels are 0.5 mg/L and 0.25 mg/L for nickel and chromium, respectively.

Passage of these waters through a column (6 mL total volume) containing AlgaSORB® resulted in effluents that were below 0.5 ppm in nickel after elution of 175-bed volumes. The nickel could be easily stripped by passage of acid through the column. However, chromium broke through rather rapidly after the passage of only five-bed volumes of the metal-contaminated groundwater through the column. This was actually what had been anticipated since other work has shown that chromium(VI) is most strongly bound to AlgaSORB® at pH 3.5 and is not bound at pH values near 7. Thus, after adjustment of the pH of another portion of these waters to pH 3.0 and passage through another AlgaSORB® column, results showed that after elution of 225-bed volumes of the chromium-bearing waters through the column, chromium content in the effluents was near or below 0.3 mg/L. Thus, these waters can be successfully treated using two AlgaSORB® columns, if the pH of the effluent from the first column is adjusted to pH 3 before passage through the second column.

D. Removal of Mercury from Contaminated Groundwaters. Bio-recovery was provided with water samples from a mercury-contaminated groundwater site. The site had been contaminated with mercury years ago through the process used to manufacture chlorine from seawater. The groundwaters contained 2-3 ppm of mercury (both inorganic and organic mercury), had a total dissolved solid content of 7,200 mg/L and contained over 900 mg/L of calcium and magnesium. Passage of these mercury-containing waters through an AlgaSORB® column (0.7 cm ID x 13 cm high) resulted in effluents which ranged in mercury content below 0.006 mg/L as determined by analysis using cold vapor generation and atomic absorption spectrometry. The customer requires effluents of below 0.01 mg/l for discharge.

These experiments show, as had earlier experiments, that AlgaSORB® is effective in removing both inorganic and organic mercury from aqueous solutions even in the presence of very high calcium, magnesium and salt concentrations.

CONCLUSION

AlgaSORB® is a biological ion exchange resin which has proved to be particularly effective in removing heavy metals from various types of wastewaters.

In the presence of high total dissolved solids AlgaSORB® is particularly effective in reducing heavy metal ion concentrations down to the parts per billion level.

Underground aquifers, leachates, mine drainages and often industrial wastewaters contain high concentrations of total dissolved solids. These total dissolved solids make it difficult and costly if not impossible to recover heavy metals by any method other than the AlgaSORB® technique.

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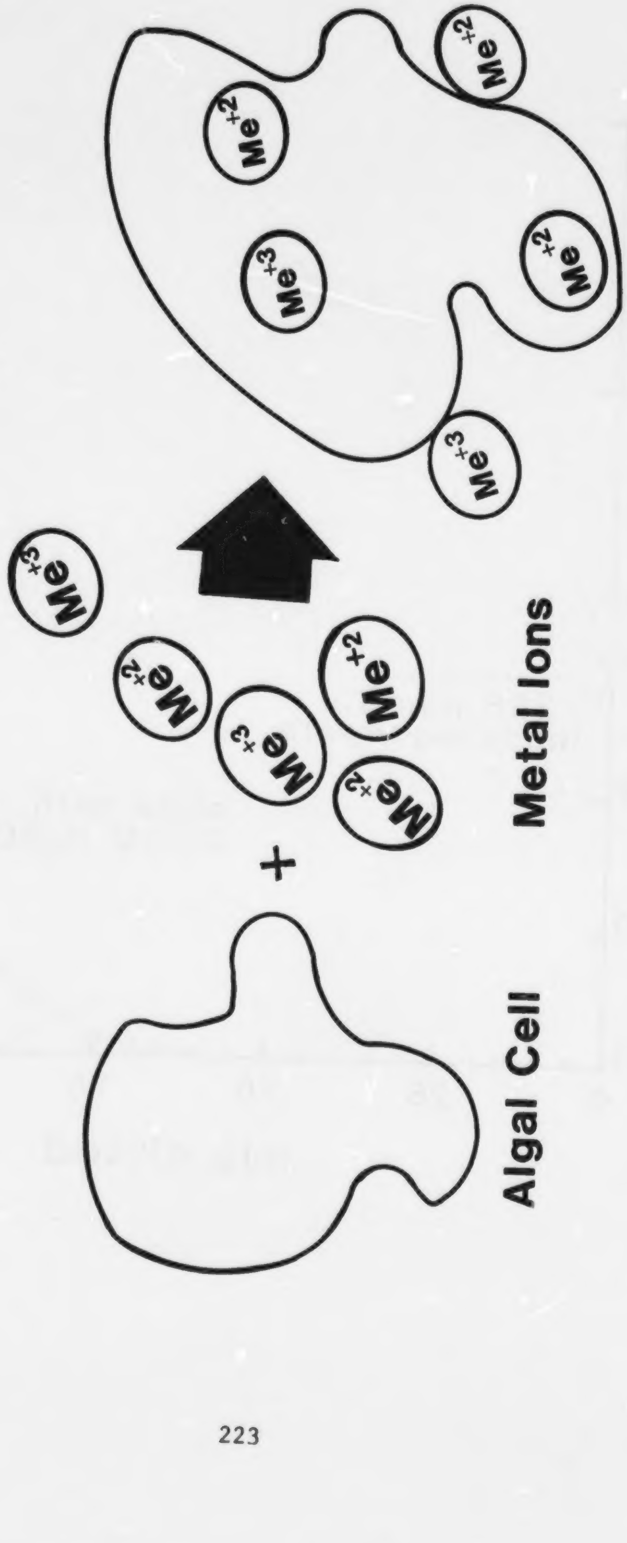
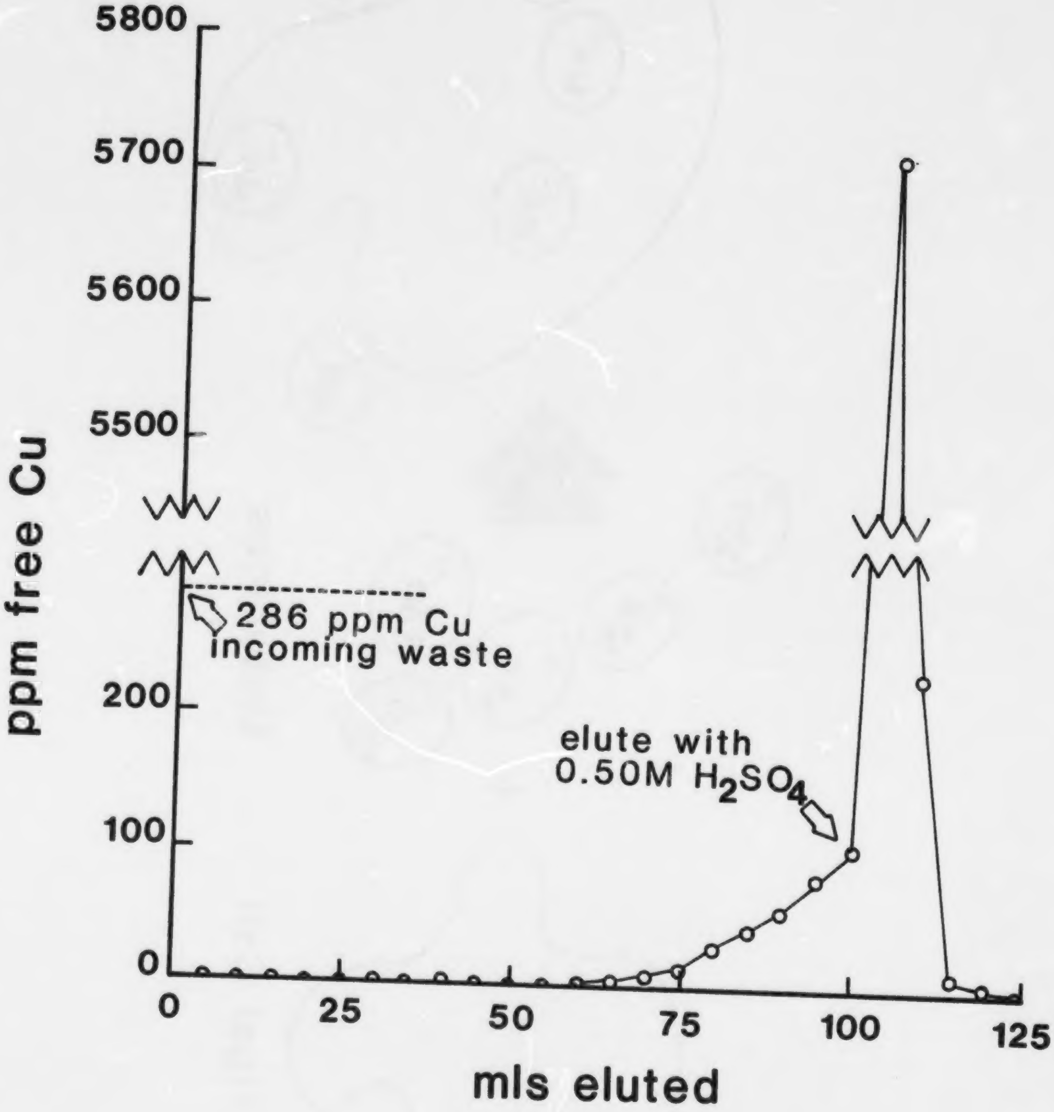
Figure Legends

Figure 1. The Reaction of Divalent and Trivalent Metal Ions with an Algal Cell. The metal ions in an aqueous solution are rapidly complexed by the biopolymers in an algal cell wall.

Figure 2. Removal and Recovery of Copper from an Ammoniacal Etch Waste Stream in a Printed Circuit Board Manufacturing Facility. The waste solution containing copper as the ammonia complex was passed through a column containing 0.5 g of AlgaSORB®. After the column became saturated with copper as evidenced by the presence of copper in the effluent (near 75 mL) sulfuric acid was passed through the column to elute the bound copper.


Algal Cell
+
Me^{+2}
Me^{+3}
Me^{+2}
Me^{+2}
Me^{+3}
Metal Ions
Me^{+3}
Me^{+2}
Me^{+3}
Me^{+2}
Me^{+2}


5800
5700
5600
5500
200
100
0
ppm free Cu
286 ppm Cu incoming waste
elute with 0.50M H₂SO₄
0
25
50
75
100
125
mls eluted

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

HAZARDOUS WASTE MANAGEMENT IN RESEARCH LABORATORIES

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ABSTRACT

Hazardous waste management in research laboratories benefits from a fundamentally different approach to the hazardous waste determination from industry's. This paper introduces new, statute-based criteria for identifying hazardous wastes and links them to a forward-looking compliance system. Geared toward the unique structural and operational characteristics of laboratories, the overall system integrates hazardous waste management activities with other environmental and hazard communication initiatives. It is generalizable to other waste generators, including industry.

After the brief, labor-intensive phase necessary to implement this system on a site-specific basis, conservative hazardous waste management decisions become routine, and new liabilities for improper disposal practices are controllable. Although only the waste identification and classification aspects of the system are outlined in detail here, four other components are defined or supported, namely:

-routine and contingency practices
-waste treatment/disposal option definition and selection
-waste minimization, recycling, reuse, and substitution opportunities
-key interfaces with other systems, including pollution prevention

All the components superficially resemble those already in place for industry, but use of the statutory definition of hazardous waste and toxicity information from material safety data sheets (MSDSs) as the basis for classifying waste hazard has far-reaching implications.

INTRODUCTION

A cornerstone of hazardous waste management in the United States is the "cradle-to-grave" concept. Once a material is identified as a hazardous waste (i.e., enters the cradle), it must be managed and tracked for its entire life, to its final disposition (i.e., to its grave). The hazardous waste determination (1) is the process for identifying hazardous waste, and the manifest (2) is the mechanism for offsite tracking. Facilities are authorized to treat, store, or dispose specified hazardous wastes, provided they meet certain regulatory and/or design criteria.

Since enactment of the Resource Conservation and Recovery Act (3)

(RCRA) in 1976 and the RCRA regulations (4) in 1980, the regulatory programs for hazardous waste have changed in significant ways. They were extended to generators of smaller quantities of hazardous waste. Uniform manifest forms were introduced and modified. Facility standards were made more stringent. Consistent with RCRA's liability provisions and reflected in the landfilling bans, even the operational definition of the regulatory endpoint has changed: the period of care is now generally recognized to extend until the hazardous waste is no longer hazardous (i.e., is treated by incineration, neutralization, etc.) and/or is no longer a waste (i.e., is recycled/reused).

While evolution of the RCRA regulatory program has been dramatic at times, its maturation in the area of identification of hazardous waste has lagged noticeably. Some changes in the hazardous waste lists and characteristics have occurred, but RCRA's regulatory (5) and statutory (6) definitions still differ greatly. This discrepancy might be less important if only RCRA's listed and characteristic items were in fact hazardous as wastes, if the Superfund (7) list of hazardous substances (8) were not nearly twice as long as the RCRA lists, if liability and costs for cleaning up contamination were not so high, and if negative public reaction to even the perception of improper disposal were not so prevalent.

It is predictable that the hazardous waste regulations will eventually be changed to better reflect the statutory definition. Some movement to expand the "cradle" is already evident in areas such as infectious wastes, radiological mixed wastes, and waste oil.

Research laboratories are representative of the type of organization that will be most affected by changes in the way in which hazardous wastes are defined. Their variable and sporadic wastestreams do not easily fit the model of the hazardous waste regulations. On the other hand, they are particularly fertile ground for application of a hazardous waste determination system that focuses first on hazardousness, then on wastes. Such a system is described herein.

PURPOSE

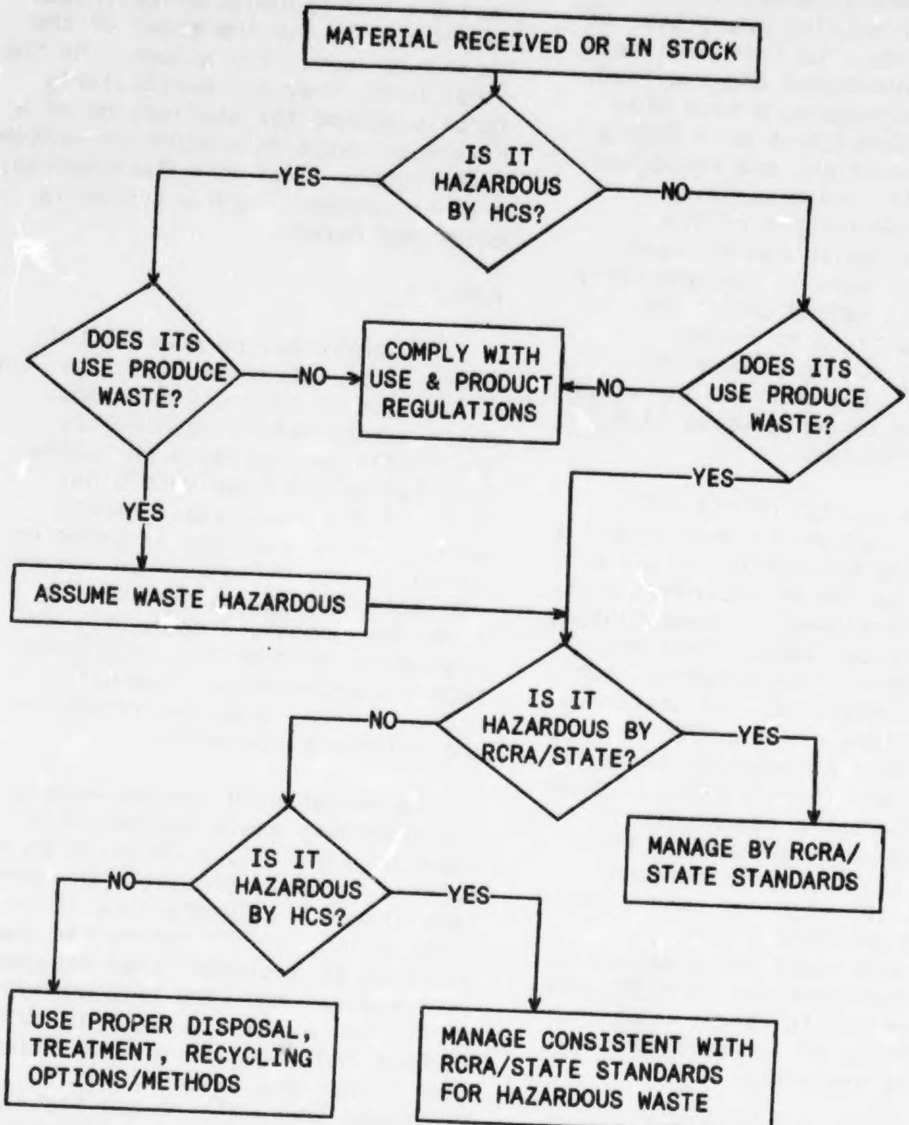
The principal purpose of this paper is to introduce, describe, and illustrate an advanced hazardous waste determination methodology applicable to the research laboratory but generalizable to other types of hazardous waste generators. The methodology is based on the statutory definition of hazardous waste and can be meshed with other management, compliance, and regulatory initiatives, including hazard communication, community right-to-know, waste minimization, and pollution prevention.

In re-defining the parameters of the hazardous waste determination as shown in Figure I, a decision on a material's "hazardousness" precedes (and drives) its waste classification, which in turn determines how it is to be evaluated then managed as a waste. Applying this methodology, the prudent manager is able to make and document science-based operational and waste-disposal decisions that will reduce liability exposure, now and in the future.

APPROACH

A four-step approach is utilized to develop and then implement this model hazardous waste

FIGURE I
DECISION TREE FOR THE MODIFIED HAZARDOUS WASTE DETERMINATION


MATERIAL RECEIVED OR IN STOCK
IS IT HAZARDOUS BY HCS?
YES
NO
DOES ITS USE PRODUCE WASTE?
NO
COMPLY WITH USE & PRODUCT REGULATIONS
NO
DOES ITS USE PRODUCE WASTE?
YES
YES
ASSUME WASTE HAZARDOUS
IS IT HAZARDOUS BY RCRA/STATE?
NO
YES
MANAGE BY RCRA/ STATE STANDARDS
IS IT HAZARDOUS BY HCS?
NO
YES
USE PROPER DISPOSAL, TREATMENT, RECYCLING OPTIONS/METHODS
MANAGE CONSISTENT WITH RCRA/STATE STANDARDS FOR HAZARDOUS WASTE

identification/management system. First, hazard classes are defined, and objective criteria are used to classify the various substances found in the laboratory. Second, the boundary between substance and waste is rigorously established, and the same criteria are applied to the wastes resulting from the use of these substances. Third, criteria and options for treatment and disposal of wastes are identified. Finally, site-specific procedures are implemented, monitored, and evaluated.

Assigning hazard classes. This step is the inventory and hazard assessment portions of the Occupational Safety and Health Administration Hazard Communication Standard (9) (HCS). The laboratory is inventoried for all chemical and biological agents. If possible, the inventory is computerized, and the database is designed to accept information on acquisition and disposal. Searchable fields in the database are used to designate each substance as hazardous or not, its hazard type, management practices required, disposal options, quantities used, and so forth.

The principal sources of data for these assessments are MSDSs and the references listed in Appendix C of the HCS. Appendices A and B of the HCS, summarized in Table I, are the criteria for the classification.

Identifying and classifying wastes. This step entails the process presented in Figure I. The underlying principle in this model is conservative and departs significantly from the RCRA approach and regulations: until specifically found to be nonhazardous, a waste that is - or contains - a hazardous chemical or biological agent (as these terms are defined by the HCS) is assumed to be a solid waste and is a hazardous waste.

A substance/material is not a waste - and so cannot be either a hazardous or nonhazardous waste - until it is no longer needed (e.g., will no longer be used), is to be discarded or disposed (e.g., to be gotten rid of, in fact or in effect), is no longer useful for its intended purpose (e.g., doesn't meet specifications), is spent (e.g., a contaminated degreaser or extraction solvent), is inherently waste-like (e.g., dirty vacuum pump oil), and/or is to be abandoned (e.g., removed from active, managed inventory), recycled (e.g., re-distilled or sent to a recycler/reclaimer), or used in a manner constituting disposal (e.g., used motor oil used for dust suppression). When one or more of these conditions is met in fact (not just by generator declaration), a waste has been generated.

The RCRA statute provides the qualitative starting point for re-defining the hazardous waste determination: a hazardous waste is a solid waste or combination of solid wastes, which because of quantity, concentration, or physical, chemical, or infectious characteristics, may cause or contribute to increased mortality, serious chronic illness, incapacitating acute illness, or a substantial present or potential hazard to human health or the environment if improperly treated, stored, transported, disposed, or otherwise managed. Many more substances than appear on the RCRA lists are hazardous by this definition.

The best available quantitative measure of RCRA's qualitative criteria (at least as far as human health effects are concerned) are the same Appendices A and B of the HCS summarized in Table I. Solutions, mixtures, and other forms in which a hazardous agent are used are also considered hazardous until explicitly found otherwise.

If the waste is derived from, or contains, a hazardous substance or

TABLE I
CRITERIA FOR IDENTIFYING PHYSICAL AND HEALTH HAZARDS

Criterion	Representative Range	Waste Hazard
Carcinogen	Proven or potential carcinogen, mutagen, or teratogen	Acute
Corrosive (bio)	Destroys or irreversibly changes living tissue	Acute
Highly Toxic	$LD_{50} \le 50$ mg/kg, $LD_{50} \le 200$ mg/kg, $LC_{50} \le 200$ ppm, $LC_{50} \le 2$ mg/l	Acute
Irritant	Reversible inflammatory effect on skin or eyes	Hazardous
Sensitizer	Allergic reaction possible in exposed individuals	Hazardous
Toxic	$50 \le LD_{50} \le 500$ mg/kg, $200 \le LD_{50} \le 1000$ mg/kg, $200 \le LC_{50} \le 2000$ ppm, $2 \le LC_{50} \le 20$ mg/l	Hazardous
Target Organ Effects	Irrevesible	Acute
	Reversible	Hazardous
Physical hazard	Combustible liquid, compressed gas, explosive, flammable, oxidizer, organic peroxide, pyrophoric, unstable (reactive), water-reactive, corrosive (chemical)	Hazardous

material (initially, as a result of chemical reaction, etc.), it is classified as a hazardous waste. On a case-by-case basis, the waste may be reclassified as nonhazardous if it is, or is no longer, hazardous by the HCS criteria. For example, use of something hazardous to make a reagent solution may yield a nonhazardous solution by virtue of dilution (e.g., glacial acetic acid for a 10 millimolar acetic acid solution), neutralization (e.g., hydrochloric acid added to neutralize a base), or reaction (e.g., acrylamide polymerization). The re-classification as nonhazardous may be based on analysis or knowledge of the process and should be documented.

If reclassification is not

appropriate, the waste must be added into the lab's hazardous waste generation figures and be managed and tracked as a hazardous waste, whether it is treated or disposed onsite, shipped offsite, or otherwise managed. If the state of nonhazardousness was reached after the substance became a waste, the process of rendering it nonhazardous is considered treatment. Depending upon the quantity and type of hazardous waste generated at the facility and other factors, a RCRA or other permit for the treatment of hazardous waste may be required.

Identification/selection of waste treatment/disposal alternatives. Feasible and site-specific preferred alternatives are identified, as are regulatory constraints/requirements and the level of risk/liability exposure management is willing to assume in the short- and long-term. Chemical supplier catalogs and Prudent Practices (10) can be valuable resources for identifying potential treatment/disposal options that may be used in many cases. However, it must be kept in mind that State regulations, local sewer-use rules, and other constraints may foreclose some of these possibilities. Management should issue specific guidance on identifying and selecting waste treatment/disposal options that are sensitive to the natural and sociopolitical environment.

Program implementation. Once the hazardous waste identification system is developed, it must next be implemented, integrated with the rest of the lab's hazardous waste management and other systems, and periodically evaluated. This process is made easier if management and individual(s) responsible for the day-to-day execution of the necessary work realize that this program has fundamentally different goals from the facility's safety and industrial hygiene initiatives: it is aimed at protecting the public and environment outside the workplace.

PROBLEMS ENCOUNTERED

The impediments to implementing this system lie in 5 distinct areas:

- the nature of research operations,
- the availability of resources,
- existing stocks of materials,
- letting wastes be wastes, and
- application of hazard information.

Nature of research operations. The work carried out in a research laboratory typically involves a number of relatively autonomous units, possibly with differing institutional affiliations, working in relative isolation without much in the way of central administrative controls. Composition of the limited volumes of waste, which are generally produced only sporadically, can vary widely, depending on research objectives and direction. Most chemicals are used predominantly in relatively dilute solutions.

Availability of resources. In recent years, negative growth in fiscal and manpower resources has been the norm. Administrative and other support services have been squeezed, and the laboratory manager and researcher are both under pressure to minimize non-research costs and administrative workload. Typically, full hazardous waste management responsibility is given to the lab's marginally-trained collateral-duty safety officer. Under these circumstances, even current RCRA hazardous waste determination requirements are not always properly met. Also, little help is available from immature and understaffed regulatory agencies still trying to catch up with hazardous waste generators who are not in the "gray areas" of RCRA.

Existing stocks of materials. A decentralized inventory of thousands of commercial and experimental compounds is commonly present, many in poor condition and in dead storage under no one's control. Labels may be missing and records of contents lost or dispersed as a result of retirements or organizational changes. Where inventory records do exist, they are typically on file cards and have not been incorporated into the laboratories' hazard communication program, so MSDSs and hazard labels are not present. Unfortunately, there is no good substitute for the labor-intensive physical inventory of the lab's chemical and biological stocks.

Letting wastes be wastes. Budget uncertainties, plan changes, personality traits, and other factors make discarding anything difficult.

Application of hazard data. Even if hazard data are available, most researchers are not trained in chemical and biological hazard identification and are cognitively unaware of any waste problems.

Taken together, these 5 problem areas tempt management into one of two extreme positions. The first can be characterized as inertia and neglect, the second as overkill. In the former, little is done before (or even after) a crisis arrives in the form of an inspector from a regulatory agency or the discovery of environmental contamination by others. In the second approach, the "quick fix" is grabbed, whatever the cost and whether or not it fits the lab's needs or situation.

RESULTS

This hazardous waste identification system takes its place beside other management systems (Table II) to ensure that conservative, informed decisions are made with respect to laboratory chemicals and the wastes resulting from their use. Application of the same hazard criteria to both materials and wastes yields a defensible consistency, a smooth transition at an important regulatory boundary, and a way to avoid legally but inadvertently producing new Superfund sites.

The system simultaneously advances the developing "pollution prevention" ethic, which is rooted in the economics of cleaning up environmental contamination. It provides real incentives for meeting the waste minimization objectives of RCRA. It mandates a conscious process at the transition point between materials and wastes.

By implementing this last link in the chain of materials and waste management and integrating it into other administrative systems, facility managers are able to assure themselves and the public that responsible and scientifically-defensible decisions are being made and documented.

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4. 40 CFR 260-280

TABLE II
MATERIALS AND WASTE MANAGEMENT SYSTEMS

System	Objectives
Hazard communication	Inform employees of chemical hazards in the workplace
Hazardous materials management	Minimize personal injury and property damage from incidents involving hazardous materials
Inventory management	Cost and overhead control
Emergency planning/ Community right-to-know	Inform public and emergency responders of hazards present
Experimental design	Logistical planning from concept to cleanup
Waste identification	Housekeeping and space utilization
Hazardous waste identification	Ensure proper handling, treatment, and disposal of hazardous wastes
Waste minimization	Cost and overhead control
Hazardous waste management	Ensure proper handling, treatment, and disposal of hazardous wastes
Recordkeeping	Documentation of activities
Emergency/contingency planning	Ensure employees know what to do in an emergency
Pollution prevention	Source reduction and recycling

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WASTE REDUCTION -- WHAT IS IT? HOW TO DO IT?

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ABSTRACT

Numerous case studies indicate that the sound management of resources results in simultaneous economic and ecological benefits. If less waste is produced, there is less potential for damage to the environment. Consequently, waste reduction is sound economically as well as ecologically. It's simply good business. However, beyond simply understanding these technical approaches to waste reduction, it is widely recognized by the experts that waste reduction is first and foremost an attitude.

The old attitude that environmental compliance costs money (and will be considered only when absolutely necessary) must give way to a new attitude that waste reduction is a sound investment which makes good business sense. Businesses need to see that they can benefit economically by complying with environmental regulations through waste reduction. Environmental protection must become an integral part of the day-to-day business decision-making process.

Since its inception, the Center for Hazardous Materials Research (CHMR), through its technical assistance program, has been assisting businesses to identify opportunities for waste reduction and to implement waste reduction programs. Through this technical assistance, essential elements for successful waste reduction were identified, which include: management initiatives; waste audits; improved housekeeping; substitute materials; redesigning equipment; recycling and reuse; and waste exchanges.

This paper goes beyond simply explaining each of the elements necessary to achieve waste reduction. Examples of waste reduction successes are provided and personal experiences related which emphasize the role of attitude changes in implementing any successful waste reduction program.

INTRODUCTION

Approaches to waste minimization are primarily low-cost, low-risk alternatives to hazardous waste disposal. Most of the approaches do not require a great deal of sophisticated technology and can be relatively inexpensive. In short, waste minimization approaches are: technically feasible, economically viable, and ecologically beneficial.

In general, any waste minimization program should include or consider: (1) management initiatives, (2) waste audits, (3) improved housekeeping, (4) substitute materials, (5) redesigned equipment, (6) recycling and reuse, and (7) waste exchange.

This paper will introduce these various elements of waste minimization. Case studies are selected which emphasize the role of attitude changes in implementing any successful waste reduction program.

PURPOSE

Over the past two decades, there has developed an increased awareness of the harmful effects to human health and the environment from uncontrolled releases of pollutants and hazardous substances. Initially, this led to a national waste management strategy which emphasized the control and cleanup of pollution by hazardous substances after they are generated and no longer serve a productive function. Now the nation is turning its attention to preventing hazardous waste problems by cutting down on the generation of hazardous waste at its source.

Many individuals and facilities have already identified and implemented waste reduction opportunities, although data suggest that current waste generation can be further economically reduced nationwide with existing technology by about 50%.[1]

However, many waste generators are still unaware of waste reduction opportunities or don't know how to go about developing their own waste reduction program. As a result, they have done little or nothing to reduce their wastes.

Much work is still needed in order to help individuals in business understand the technical approaches to waste reduction and identify waste reduction opportunities in their operations. However, beyond simply understanding the technical approaches, waste reduction is first and foremost a problem of attitude. Every successful waste reduction program begins with an attitude change regarding how we view the generation and management of waste.

APPROACH

Research was conducted to identify the key elements of a successful waste reduction program. These key elements were reviewed and further developed in the conduct of a statewide waste reduction technical assistance program which included on-site audits, training seminars, and other interactions with individuals, in industry and small business, who were concerned about reducing the wastes they generate.

Numerous case studies on successful waste reduction efforts were collected and reviewed. Several case studies were selected and summarized which emphasize the role of attitude changes.

PROBLEMS ENCOUNTERED

Centralized sources of information on waste reduction were lacking, and problems were encountered in collecting information on waste reduction technologies. There is insufficient dissemination of information regarding reduction methods or successful approaches to developing and implementing facility specific waste reduction programs.

Because of the need to sort through the vast amount of old and new information becoming available, technical assistance is needed by all generators to fully understand options, costs, and benefits of various waste reduction strategies. Technical assistance programs are needed which can also serve as clearinghouses for technical and relevant regulatory information.

RESULTS

Numerous case studies 2-7 exist which indicate that the sound management of resources results in simultaneous economic and ecological benefits regardless of the size of an organization. These case studies show that: (1) waste reductions can range from 20% to 98%; (2) payback periods for waste minimization investments typically range from immediate to 5 years; and (3) firms which handle fewer hazardous materials reduce hazards to their workers and the environment--and experience fewer longterm liability and victim compensation claims.

The Role of Attitudes

However, review of these case studies, combined with experiences in performing waste reduction audits, training programs, and other interactions with individuals in the business community, clearly indicates that attitudinal change is at the heart of expanding voluntary waste reduction practices.

The old attitude that environmental compliance costs money must give way to a new attitude that waste reduction can be a sound investment and makes good business sense. Businesses must see that they can benefit economically by complying with environmental regulations through waste reduction.

The old attitude that environmental protection is best achieved through "end of pipe treatment" must give way to a new attitude that environmental protection is best achieved by reducing waste generation at the source.

The old attitude that waste is inevitable must give way to a new attitude that waste reduction is a dynamic opportunity contingent on a host of changing technical, economic, and institutional factors. Substantially more waste reduction is currently feasible and more will become feasible in the future.

Basic attitude changes take time, and waste reduction cannot be achieved overnight. However, the process of changing attitudes must begin immediately, and environmental protection through waste reduction must become an on-going, integral part of the day-to-day business decision-making process.

The remainder of this paper sets forth essential elements of a waste reduction program, which when combined with basic attitudinal changes, will result in successful reduction of waste generation.

Developing Management Initiatives

The commitment to waste minimization must come from the top--the management of a business or organization. Management initiatives are vital to the success of any waste minimization efforts.

The following two management actions are crucial to a successful waste minimization program. (1) Communication--Management must make all employees aware of the waste minimization effort. (2) Incentives--Management should provide incentives for the development of useful waste minimization ideas just as incentives are used to boost employee productivity.

Although a waste minimization commitment should begin with management, the employees are often able to suggest improvements in the day-to-day operations of the business. The new management initiatives should foster the following elements of waste minimization success: increased awareness and attention to hazardous chemicals; motivation to change old work patterns; knowledge of options for change; and willingness to innovate and change. Another important management tool is employee training.

Waste Audits

The waste audit is the most basic of all of the approaches to waste minimization. The waste audit tracks hazardous waste by monitoring all of the waste which is produced at a place of business to learn where it was generated. One can determine where hazardous materials are used and where materials are being wasted. As a result, areas of a business that produce waste may be discovered which had not been recognized before the audit.

The waste audit can be divided into the following six steps: (1) identifying hazardous substances in waste or emissions; (2) identifying the sources of these substances; (3) setting priorities for various waste reduction actions to be taken; (4) analyzing some technically and economically feasible approaches to waste minimization; (5) making an economic comparison of waste minimization and waste management options; and (6) evaluating the results.

The waste reduction audit is a systematic and periodic survey of a company's operations and is designed to identify areas of potential waste reduction.

Improving Housekeeping

Improved housekeeping, or "good operating practice," is the simplest waste minimization practice. Improved housekeeping relies on using common sense and is often the most effective first step toward waste reduction.

Good housekeeping practices involve the procedural or organizational aspects of a manufacturing process and include elements such as: inventory control, waste stream segregation, material handling improvements, spill and leak prevention, improved scheduling, and preventive maintenance.

One relatively simple housekeeping method is waste segregation. In many cases, segregation of wastes allows for certain wastes to be recycled or reused. For example:

- **In a business using both chlorinated and nonchlorinated solvents, these waste types should be kept separate.**

- **At a printing company, waste toluene from printing press cleanup can be eliminated by segregating this solvent according to the color and type of ink cleaned from the press. Each segregated batch of toluene can be reused for thinning the same color ink.**

Improved labeling allows employees to know precisely what a container or pipeline holds and guards against accidental spills and unnecessary use--both a waste of materials. All substances used in the workplace should be properly labeled. In additional, all wastes, once segregated, should be labeled as well. This procedure helps to ensure safe handling of wastes, and can point out containers of waste which have the potential for recycling, reuse, or even resale.

Substituting Materials

A waste audit may identify specific materials within a business which are producing hazardous waste. If this is the case, it may be possible to find a substitute material which is less hazardous. Although material substitution is only applicable in certain situations, it can prove to be an efficient waste minimization approach. For example:

- **A painting business uses a hydrocarbon solvent (toluene) for cleanup of hydrocarbon-based paint. By switching to water-based paint, water can be used for toluene during cleanup.**

- **Water-soluble cleaning agents can often replace organic solvents or degreasers. One company did this and successfully reduced its 1,1,1-trichloroethane use by 30%, resulting in a $12,000 annual savings.**

- **ITT Telecom reduced the quantity of waste solvents they generate by merely replacing a solvent-based, photo-resist system with an aqueous-based system. The new system reduces hazardous waste generation and also improves product quality while reducing production time.**

Technology Modifications

In many instances, technological modifications or material substitutions are also very effective in minimizing wastes. Some products can be manufactured by two or more distinct processes, and one process may produce less hazardous waste than the other. Modifying equipment within a given process is another way to reduce waste generation.

Technological modifications can be generally categorized as: process modifications, equipment modifications, process automation, changes in operation settings, water conservation, and energy conservation.

Production processes may be responsible for the production of hazardous waste. Old or inefficient processes could be sources of hazardous waste. By changing to a newer, more efficient process, a company could decrease the amount of waste it generates. In addition, many companies can experience improved production capacity and product quality and realize savings in expenditures for utilities and raw materials. For example:

- o In printed circuit board manufacture, the use of screen printing for image transfer instead of photolithography eliminates the use of developers.
- o By replacing a solvent-based painting system with a water-based electrostatic immersion painting system, the Emerson Electric Company has reduced waste solvent and paint solids generation by over 95%.
- o A chemical company reduced phenol resin waste by 95%. Old tank cleaning procedure (filling with water which was then discharged for treatment) was replaced with a two-step process where an initial small volume rinse produces a concentrate which could be recycled as raw material. Second rinse produces waste stream with reduced phenol resin content.

Process modifications often entail subsequent equipment modifications. Equipment modifications accomplish waste reduction by reducing or eliminating equipment-related inefficiency. An equipment modification leaves the production process intact and also unchanged because it modifies only the equipment which comprises the process. For example:

- o A simple dragout recovery system was installed on a nickel plating machine. Less than $1,000 was invested for a storage tank, which saved the firm $4,200 worth of nickel per year and reduced nickel sludge generation by 9,500 pounds per year.

Process automation involves the use of automatic devices to assist or replace human employees. Automation can include monitoring and subsequently adjusting process parameters by computer or mechanically handling hazardous substances. Waste minimization is accomplished by reducing the probability of employee error (which can lead to spills or off-spec products) and by increasing product yields through the optimum use of raw materials.

Often the generation of hazardous waste may not be the fault of the equipment. Instead, the fault may lie in the way in which equipment is set to operate. These are often the most easy and inexpensive of equipment changes. For example:

- o Many spraying processes operating at decreased pressures have less overspray and subsequently less waste.
- o In formulating their cyanide copper plating baths, the Standyne Company determined that lower chemical concentrations can be used. By running the potassium cyanide concentration at 2.5 ounces per gallon, instead of 3.5 ounces, the cyanide dragout concentration was reduced by 28% without any adverse effect on plating quality.

Most equipment has optimum settings at which it operates most efficiently. By determining the optimum settings for certain parameters (such as optimum temperature and pressure), less waste is generated as a by-product.

Although not as significant as other approaches, water conservation can have an effect on minimizing hazardous waste generation. For example:

- **By reducing the amount of water used for washing some organic chemical products, companies can lower the amount of waste water which must be pretreated before disposal.**

Energy conservation minimizes the waste associated with the treatment of raw water, cooling water blowdown, and boiler blowdown. In addition, lower energy usage means a reduction in the generation of ash and other wastes associated with combustion. Energy conservation can be accomplished through a series of heat exchanges within the production process.

Recycling and Reuse

Recycling and reuse of hazardous wastes can be a very economical undertaking. Many companies have discovered that the cost of installing on-site recycling equipment can be quickly recovered, and future profits gained, by savings in waste management and raw material costs. For example:

- **A pesticide manufacturer generated pesticide dust from two major production systems. The firm replaced the single baghouse with two separate vacuum-air-baghouse systems specific to the two production lines for $9,600. The collected material was recycled to the process where it was generated. The firm has eliminated over $9,000 annually in disposal cost, and they estimate that the recovered material is worth more than $2,000 per year.**

- **The Rexham Corporation facility in Greensboro, North Carolina, installed a distillation unit to reclaim n-propyl alcohol from waste solvent for a total installed cost of $16,000. The distillation unit recovers 85% of the solvent in the waste stream, resulting in a savings of $15,000 per year in virgin solvent costs, and in a $22,800 savings in hazardous waste disposal costs.**

In addition, there are many off-site recyclers who will take a company's waste, recycle it, and sell the refined product back to the company at a price significantly less than the cost of virgin material. Additionally, that company will not have to entail waste disposal costs.

- **The Hamilton Beach Division of Scovill, Inc., operation requires the solvent 1,1,1-trichloroethane to degrease metal stampings. Ashland Chemical Company was contracted to recycle the waste by distilling 1,1,1-trichloroethane. Substituting the recycled solvent for the virgin product has reduced Hamilton Beach's overall raw material costs by $5,320 per year. Scovill also eliminated all of their previous waste disposal costs, estimated to be about $3,000 per year.**

Participating in Waste Exchanges

Waste exchanges are networks of businesses which attempt to find markets for the wastes they generate. Remember that hazardous waste to one business can be a valuable resource to another. The exchange attempts to match one business waste with another business raw material requirements. Small businesses can also find excellent recycling opportunities through such organizations. Often a "buyer" company is able to purchase, recycle, and subsequently reuse another's waste. In this way, the buyer is able to save on raw material costs, and the hazardous waste generator is able to market a new product as opposed to disposing a hazardous by-product.

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We also extend our appreciation to those leaders of industry who provided information on their industrial processes and on the ways they have minimized their wastes.

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PAINT REMOVAL STRATEGIES EFFECTIVE IN REDUCING WASTE VOLUMES AND RISKS

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ABSTRACT

As new paint and surface coating formulations are developed, it becomes increasingly difficult for paint and maintenance personnel to remove surface coatings in preparation of product finishing. A number of new paint stripping technologies have emerged to keep up with advances in the paint technologies, as well as, the issues dealing with environmental risks, workplace safety, rising disposal costs, new multi-media control standards and increased productivity demands. Improvements in chemical resistivity are directly affecting chemical usage rates, and the pollutant loadings comprising air, water and solid wastes. The paint stripping inefficiencies are dictating new strategies geared at waste minimization and optimum performance without jeopardizing the workplace and the environment. The strategic evaluations are resulting in controversy in the aircraft industry over the use of new stripper formulations versus dry paint removal technologies. The strategic options are weighed in the context of paint removal performance efficiencies and waste generation.

INTRODUCTION

The paint and surface coatings industries are recognizing record demands for shipments of new products employed by numerous industries requiring applications of architectural coatings, product coatings and special-purpose coatings. Research endeavors have revolutionized the quality and performance of surface coatings. A number of the major plastics and automotive materials suppliers, including, but not limited to: PPG, BASF, Dow, DuPont, Mobay and ICI continue to invest millions in improvements to the constituents comprising the formulations in an effort to reduce volatile organics causing environmental and safety concerns while improving exterior appearance, durability, chemical resistivity and overall applications.

A number of paint applications for example the re-painting of aircraft, utilize a blend of surface coatings that are inferior in terms of chemical resistivity. The chemical resistivity properties of many of the thermosetting acrylics, catalyzed epoxies and polyurethanes are creating problems for individuals responsible for correcting poor quality finishes, removing surface coating formulations, and preparing surface substrates for repainting. With the aircraft industry repainting is a critical step in the overall maintenance of an aircraft displaying poor appearance and/or excess coatings influencing fuel consumption. Many of the conventional paint removal formulations can remove the new coatings at the expense of using excess labor and chemicals while creating increased loadings of hazardous pollutants in air emissions, waste waters, and solid residues.

There are a number of new chemical formulations, some of which have eliminated the use of chlorinated solvents, which have recently emerged in response to many of the paint removal issues. Their performance is dictated by the chemistry of the coatings, the standard operating protocol in terms of application, and the properties of the substrate. Several alternatives have also emerged which utilize dry systems as a means of breaking the bonds holding the paint to the substrate. Other strategies have focused on mechanical and application improvements which suppress volatile organics as a means of reducing exposure and pollution control requirements. These new formulations and paint removal systems are critical to the reduction of environmental and OSHA concerns.

PAINT CONSTITUENTS INFLUENCING WASTE GENERATION

The quality and performance of the constituents comprising paints continue to be a prime focus of many industrial research endeavors. The resulting paint formulations directly, as well as indirectly, influence the quantities and characteristics of wastes generated by paint removal operations.

Before a paint removal system is selected and a waste management strategy is developed, it is important to identify the constituents comprising exterior coatings and the likelihood that their properties will influence the hazards inherent to waste byproducts.

Many volatile solvents used in commercial paint formulation are being phased out and, in some cases, totally eliminated. The solvents generally do not effect the quality of paint residues removed by chemical stripping, since the major portion are volatilized during the painting cycle. Among the technologies improving durability and chemical resistivity of surface coatings as well as minimizing air emissions is the process of polymerizing polyester coatings for powder coatings. The oven cured powders significantly reduce many of the environmental hazards inherent in paint by the fact that the processes do not emit volatile organics and they lend themselves to easy maintenance eliminating overspray disposal problems. The powdered coatings, while not totaly applicable at this time to the aircraft industry, may create additional problems with paint removal as a result of their improved resistivity properties.

The paint chemistry will provide valuable insight into the most practical strategy for paint removal. Many of the pigments, inorganics as well as organics, can contribute to the pollutant loadings typically found with paint residues and wash solutions. The age of the coating can influence the properties of the residual pigments in terms of their solubility in water, as well as leaching solutions. Many of the new formulations of pigment display low water solubilities and their impact in terms of leachability, is minimal in comparison with some older paint systems; for example, coatings using red lead. Many of the surface coatings are formulated with resins that are resistant to an array of aqueous and organic-based chemicals.

For the most part, the resins have good to excellent resistivity to acids, alkalies, solvents and oxidizers. As such paint formulations will directly influence the selection of an appropriate stripper.

Considering the variables associated with the resistivity of surface coatings, the following factors should be considered in terms of optimizing stripper performance including; the type of film formed, the thickness of the coatings, the type of surface applied, the primer used, the type of pigment, the chemical stripper used, dwell time, temperature and method of stripper application and the age of the coating.

CHEMICAL FACTORS INFLUENCING STRIPPING PERFORMANCE

The performance of coatings/paints not only depends on the resistivity properties, but also to a greater extent on their adhesion properties. The paint stripping formation has to take into account both the capability of distracting the integrity of paint films and the ability of destroying the adhesive forces between coatings and substrate. The formation of adhesion bonds is due to not only the close range atomic interaction at the interface, but also to interdiffusion at the interface on electrostatic interaction. Various types of interfacial forces including chemical bonds such as: ionic, covalent, and metallic bondings, and intermolecular forces such as hydrogen bonds, dipole-dipole, dispersion, dipole-induced dipole have been identified. If the interfacial properties between coating and substrate can be altered, the adhesive forces between coating and substrate may also be weakened. The weakening of the adhesive forces will enhance the efficiency of paint removal.

Paint stripping technologies generally rely on physical and/or chemical mechanisms. The physical methods mechanically destroy the bondings and abrade the coating from the substrate in addition to utilizing differences in physical properties between coating film and substrate to break various bondings. The chemical methods utilize the properties of the strippers, such as solvency, oxidation and swelling to chemically attack the integrity of the coating film, while indirectly affecting the interfacial properties which can break the adhesive bonds.

There are numerous manufacturers and suppliers of chemical strippers, generally categorized as: alkaline, acid, and solvent-based. Alkaline strippers will generally break the ester linkages, however, they are not able to remove pigments. As such, various additives, including solvents, are added to improve performance. Acid strippers rely on chemical destruction, i.e., oxidation or dehydration, of the paint constituents. Acids will generally solubilize the pigments, open the coatings and remove the surface oxides, resulting in a destruction of the adhesive bond of coating to substrate. Inherent corrosion hazards must be considered prior to using acidic formulations. The solvent-types generally work by dissolving the paint, however, redeposition is a problem.

Methylene chloride-based strippers are generally viewed as the most effective strippers for removing polyurethane and epoxy types of paint without damaging the surface. As illustrated on Figure 1, methylene chloride will penetrate the coating, swelling it to a volume as much as ten times of the original film. Penetration is made possible as a result of methylene chloride's small molecular size as well as its polarity. The swelling of the film builds up pressure on all directions and the pressure can be relieved only in the direction directly away from the substrate.

As noted in Figure 1, the tensile strength is developed because of difference of swelling characteristics between coating film and substrate. To promote the rate of film swelling, cold strippers can be enhanced by the addition of various acids, alkalis, amines, and special solvents or agents. Acids may break the adhesive bond by dissolving surface oxides. Wetting agents (or penetrants) can increase the stripping rate by allowing more rapid penetration of the film. The paint stripping begins most rapidly at the edge or at flaw areas of the surface, where the penetration is easiest. The wrinkling and blistering will proceed from these areas until the entire film is effected. If there are no such areas, the wrinkling or blistering can only proceed by a slower penetration of the stripper through the surface of the film. One major drawback of the methylene chloride stripper is the evaporation loss of solvents which not only makes the stripping operation inefficient, but also results in environmental pollution problems. Although the evaporation loss can be retarded by using evaporation retarders such as water or wax seals, this loss just cannot be eliminated completely. Upon application of the evaporation retarders, the wax crystallizes out to form a film on the surface, retarding the evaporation of solvents. The epoxy-based paints typically have a strong resistivity to alkaline-based methylene chloride formulations. Epoxies, like the alkali-resistant coatings, often respond to the acidic paint removal formulations which are able to break the ether linkage.

In terms of projecting waste generation, the solvent-based formulations can contain significant concentrations of other inorganic and organic constituents serving as cosolvents, activators, thickeners, penetrants and evaporation retarders. Some of the specific constituents comprising these formulations are methanol, toluene, sodium chromate, ammonia, bentonite, metallic soaps, polyacrylate esters, cellulose acetate, ethyl cellulose and various waxes. The volatility and water solubility of these constituents will vary significantly. For example, some industries use water to remove large surface areas treated with stripper. Depending on the quantity and characteristics of the product rinse solutions it is conceivable that the volatile fraction and phenol can be detected at concentrations varying by an order of magnitude. The pollutant loadings will have a major effect on treatment requirements.

Besides methylene chloride based formulations, a number of chemical manufacturers are developing for industrial use non-halogenated formulations which are proving attractive in terms of reducing risks and disposal problems. The physical and chemical methods are compared in the next section.

ALTERNATIVE STRATEGIES FOR PAINT REMOVAL

Figure 2 is a summarized logic flow chart depicting some of the existing and new strategies for removing paint from aircraft.

Plastic media blasting, cryogenic stripping, CO_2 blasting and laser beam paint removal are among the new technologies which rely on physical paint removal mechanisms eliminating the usage of chemicals posing potential environmental hazards and risks to human health. Some of the unique features associated with each waste minimization strategy are summarized as follows:

1. Cryogenic techniques use extremely cold temperatures to cause paints to be brittle, allowing for effective debonding by non-abrasive plastic media. The technology, which is principally supplied by Air Products Co., has been applied to an array of paints including powdered coatings. This option is generally used to remove paints from equipment which has a build-up of coatings on the surface. Among the documented advantages are: its efficiency and amenability to processing at high throughputs; its elimination of hazardous chemicals; and the low likelihood of substrate damage. There are some disadvantages which require evaluation including: the inefficiencies in removing urethane and epoxies;

mechanical limitations decline with large surface areas and thin-film coatings; and the costs. The reaction in potential air emissions concerns is significant.

2. Plastic media blasting has been receiving increased attention in terms of paint removal amidst controversy over potential damage to structural integrity. For several years, PMB has generated performance data substantiating its use for paint removal. The technology uses plastic medium particles, activated by compressed air to physically abrade the paint off the substrate. This option has demonstrated wide applicability to substrates not sensitive to structural damage. The processes are apparently cost competitive with chemical stripping methods, however, there are arguments disclaiming this benefit. The process does eliminate the use of chemicals, however, the resulting solid wastes still require proper disposition. Standard operating controls are very important in terms of preventing structural damage.

3. The laser paint stripping technique is still in the developmental stage. The technology, using high energy photons from the laser, causes bond scissors in the coatings with significant increase in volume causing the coatings to be blown away from the substrate. The elimination of chemicals, excess labor and equipment prepartion are among the advantages to this option. Substrate damage, control development, excess costs and the lack of commercial units are among the disadvantages.

Source control strategies can focus on the development of new paint stripping formulations or in-plant source segregation strategies that optimize the reduction of waste volumes as well as pollutant loadings. There are considerations associated with source control strategies, including but not limited to:

- Alternative, non-halogenated, paint stripping formulations may be more costly, dependent upon heat, and may not be as effective in removing some of the combined coatings, in particular urethane epoxies.
- Alternative commercial formulations of paint strippers which vary in chemical content, specifically methylene chloride, do exist; however, each formulation requires evaluation in terms of stripping performance and retardants effective in attenuating air emissions.

- The potential for mechanically suppressing and/or containing volatile organic emissions, reducing toxic loadings and the magnitude of air flow requiring abatement.
- Modifying standard operating protocol in a manner that reduces dwell time, while improving stripping performance efficiency.
- Modifying material handling practices in a manner that calls for the removal and collection of paint residuals before the units are subjected to water rinse applications.

The segregation alternatives can have a major impact on the characteristics and pollutant loadings of the resulting waste by-products. The trade-offs associated with these source segregation alternatives need to consider the potential likelihood of water soluble stripper constituents being attenuated in wastewater treatment sludges or residuals, precluding landfills as a viable disposal option.

Among the commercially available substitutes are stripper formulations replacing methylene chloride with either N-methyl-2-pyrrolidone (M-Pyrol) or dibasic esters.

M-Pyrol is a versatile solvent that has found applicability as a prime constituest in non-halogenated paint stripping formulations. M-Pyrol provides a number of properties which are viewed as advantageous in terms of reducing hazards including; its high flash point, low vapor pressure (0.29 mm Hg) selective solvency, chemical stability, chemical stability and biodegradable properties. Among the disadvantages warranting further evaluation are; the costs of using the formulations (generally higher in comparison to conventional formulations), slower penetration rates and the potential requirement for heat.

Dibasic esters is used as an active ingredient in paint formulations and industrial cleaners. The product does not require chlorinated solvents and it has a flash point of >100° C, a low vapor pressure, low hazard potential and ideal miscibility properties with other solvents. Among the disadvantages are: its high molecular weight; which hinders penetration rates, and the fact that it is not a universal solvent for all hydrocarbons.

There are also a number of commercially available strippers, each offering variable chemical formulations. The variability in feedstock characteristics will have a direct bearing on the volumes and characteristics of waste by-products.

In reviewing the chemical options it is important to keep in mind the operations entailed with paint removal. If a water spray or rinse is employed for this purpose there is a good likelihood of detecting many of the inorganic and organic stripper constituents in the resulting wastewater. The concentration of methylene chloride and phenol in the changes in hazardous waste definition and treatment performance, the practice of combining the resultant solid and liquid wastes could culminate in treatment residues which are characteristically more hazardous and difficult to manage than the wastestreams which were originally generated.

The paint stripping operations relying on volatile solvents are faced with a major portion of their waste being released as air emissions. Future standards are expected to regulate air emissions from paint stripping operations, most likely dictating air abatement standards. The pollutant loadings in air emissions can be significantly influenced by changes in feedstock forumations, mode of stripper application, dwell time, paint removal practices and mechanical, as well as chemical suppressants. These control strategies may reduce loadings and the degree of control, but they do not eliminate risks and liabilities.

There are a number of new chemical formulations emerging in this market. New standards in the work place will magnify industry's search for substitutes as long as productivity and product quality are not adversely impacted. The performance record of new (non-halogenated) chemical formulations will enhance the need for changes in feedstocks since regulatory and competitive edge factors remain critical factors.

resulting rinsewaters could range between 1000 - 5000 ppm to 50 - 500 ppm respectively. Segregation practices and chemical usage rates can have a direct effect on the resulting pollutant loadings. In addition the resulting reduction in loadings achieved with source segregation can significantly reduce capital needs for example with air stripping systems as well as with wastewater treatment systems. As an illustrative example of how the wastewater pollutants can influence compliance status Figure 3 provides a summarized profile of paint stripping rinse water characteristics. The constituents are cross-referenced with pertinent regulatory listings (existing and future) as a mechanism for prioritizing risks and the requirements for source substitution and/or segregation. Multi-media transfer problems associated with the rinse process as well as the treatment by-products of the wastewater can be prevented or minimized by instituting an awareness program addressing feedstock contents and materials transfer.

SUMMARY

Data substantiates the fact that the chemical content of paint stripping feedstocks are the primary source of contaminants in the multi-media wastes resulting from operations dictating the removal of various types of paint and coatings. Without segregation, typical standard operating protocol can magnify environmental concerns by increased waste volumes and pollutant loadings. With regulatory

Alternate "dry" stripping technologies are proving very promising in that they eliminate the reliance on chemical formulations, thus significantly reducing resulting waste volumes and characteristics posing concerns dealing with hazard and mobility. Cryogenics and plastic media are among the technological advancements warranting further evaluation.

Each strategy has distinct advantages and, to a certain extent, disadvantages which require close examination from an economic, regulatory and performance perspective.

One of the prime factors that will be quantified as part of this assessment deals with the reduction of pollutant loadings and their associated risks and liabilities. As each strategy is weighed and prioritized, the chemical content stands out as one of the prime decision factors over time.

Disclaimer

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FIGURE 1

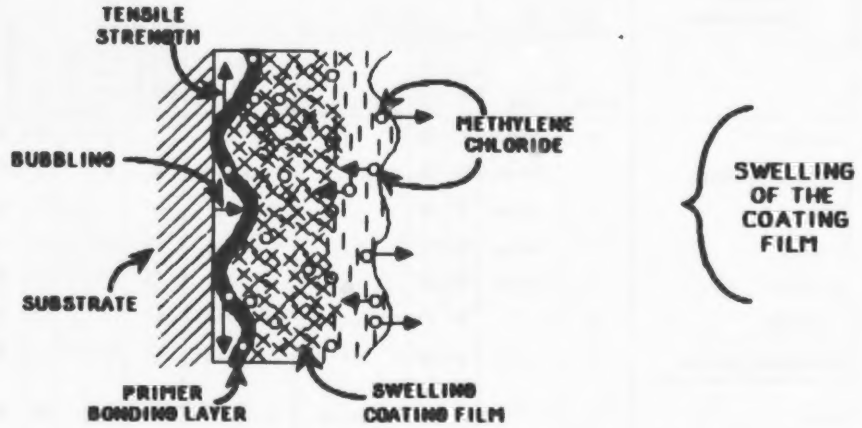
TENSILE STRENGTH
METHYLENE CHLORIDE
BUBBLING
SWELLING OF THE COATING FILM
SUBSTRATE
PRIMER BONDING LAYER
SWELLING COATING FILM

FIGURE 2

SUMMARY OF OPTIONAL TECHNICAL STRATEGIES FOR REMOVING PAINT

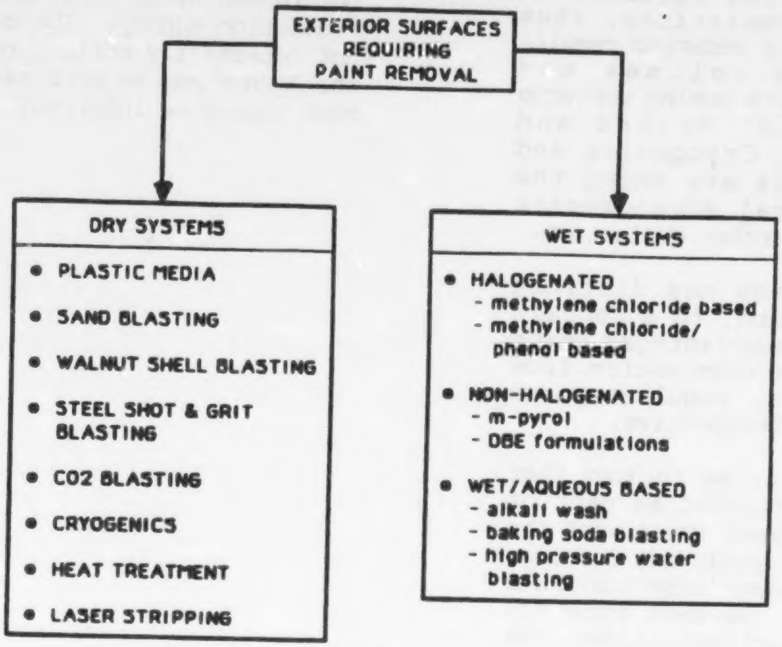
EXTERIOR SURFACES
REQUIRING
PAINT REMOVAL
DRY SYSTEMS
• PLASTIC MEDIA
• SAND BLASTING
• WALNUT SHELL BLASTING
• STEEL SHOT & GRIT BLASTING
• CO2 BLASTING
• CRYOGENICS
• HEAT TREATMENT
• LASER STRIPPING
WET SYSTEMS
• HALOGENATED
- methylene chloride based
- methylene chloride/phenol based
• NON-HALOGENATED
- m-pyrol
- DBE formulations
• WET/AQUEOUS BASED
- alkali wash
- baking soda blasting
- high pressure water blasting

FIGURE 3

A PROFILE OF WASTEWATER PROPERTIES AND APPLICABLE REGULATORY LISTINGS

PRIMARY CONTAMINANT	MOBILITY		TOXICITY			OSHA PEL (TWA)	APPLICABLE REGULATORY LISTING GOVERNING CONSTITUENT MANAGEMENT					
	WATER	AIR	ACUTE	CHRONIC	CARCINOGEN		TCLP LISTED F001-F005 WW/OTHER SOLVENTS	TCLP PROPOSED CHARACTERISTICS	EP TOXIC	APPENDIX IX	HAZARDOUS SUBSTANCE LIST	APPENDIX III
TOLUENE	0	22 mm	●	●	○	200 ppm	A	D	○	●	●	○
METHYLENE CHLORIDE	1	350 mm	●	●	Probable	500 ppm	B	E	○	●	●	●
METHANOL	4	97 mm	●	●	○	200 ppm	C	○	○	○	●	○
ETHANOL	4	40 mm	●	○	○	1,000 ppm	○	○	○	○	○	○
AMMONIA	3	>1 atm	●	●	○	50 ppm	○	○	○	○	●	○
CHROMIUM	NA	○	●	●	○	0.5 mg/m3	○	F	F	●	●	○
HEXAVALENT CHROMIUM (AS SODIUM DICHROMATE)	3	○	●	●	○	0.1 mg/m3	○	○	○	○	●	○
LEAD	1	○	○	●	Suspected	50 ug/m3	○	F	F	●	●	○
ZINC	1	○	○	○	○	○	○	○	○	●	●	○

CODE
0 - Insoluble
1 - Slightly Soluble
2 - Moderately Soluble
3 - Very Soluble
4 - Miscible

● - Applicable
○ - Not Applicable

A - 1.12/0.33 mg/l
B - 0.2/0.98 mg/l
C - 0.25/0.75 mg/l
D - 14.4 mg/l
E - 8.6 mg/l
F - 5.0 mg/l

TREATMENT AND RECOVERY OF HEAVY METALS FROM INCINERATOR ASHES

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ABSTRACT

High levels of potentially leachable toxic metals such as Pb, Cd, and Cr, in the ash residues require consideration of treatment technologies prior to disposal or utilization of the ashes in other applications. Extraction studies revealed information on the leaching characteristics of the ashes and on the ability of the extraction solutions to separate these metals from the ash matrix. The kinetics of the Pb, Cd, and Cr extraction were determined through a series of batch extraction studies. The specific incinerator design and the equilibrium conditions strongly influenced the ash matrix and the extraction kinetics. Recovery of the metals from the waste extract solution was accomplished utilizing electrochemical plating techniques. A laboratory scale pilot plant was designed to continuously treat ash residues at a rate of 1 kg/hr through extraction and electrochemical recovery techniques. Initial pilot plant operational study results are presented.

INTRODUCTION

Due to decreasing available landfill space, the minimization of the amount of solid materials requiring disposal is imperative. The incineration of municipal solid waste (MSW) results in a 90% reduction in volume and 75% reduction in mass, as compared to direct MSW disposal [1]. However, heavy metal concentrations extracted from MSW ashes were found to exceed the Extraction Procedure Toxicity test (EP Tox) limits [2]. The EP Tox test is the procedure established by the United States Environmental Protection Agency (USEPA) in testing for leachable inorganic species from solid wastes. The leachability of heavy metals from MSW ash residues must be considered prior to disposal or utilization of these materials.

Extraction studies employing ash obtained from several resource recovery facilities provided insight to the leaching characteristics of the ashes and the dependency on the extractant solution composition [3,4]. The anion and cationic effect of the extractant salt solutions were investigated, as well as the pH of the system. A 1 N NaCl solution (aqueous), acidified with HCl, was found to be the most effective in heavy metal extraction. The kinetics of the leaching process were defined and the electrochemical recovery of the metals in solution was investigated [5]. These studies led to the design and operational parameters of a laboratory scale pilot plant, incorporating continuous extraction, separation, and electrochemical processes. The results of the initial pilot plant operation experiments are presented in this paper.

Incinerator Designs

Two incinerators were sampled for ash residues, one located in Canada and one in Massachusetts. The Canadian incinerator includes a three tiered vibrating grate primary combustion chamber and a secondary combustion chamber. Solids are fed to the combustion chamber using a hopper and have about a three hour residence period. Sixty percent of the combustion air is provided as underfire air, the remainder of the air is introduced above the burner beds. A full waterwall is provided in the incinerator. A shell and tube heat exchanger cools down the exit gases and fly ash, and separation of the gases and fly ash occurs in an electrostatic precipitator.

The Massachusetts incinerator utilizes a baffled, three tiered combustion chamber in which the solids are periodically moved tier to tier via a hydraulic ram. The solid residue is quenched in the ash pit and then removed, while the gases and fly ash pass through a secondary combustion chamber. The ash is separated from the combustion gases utilizing a charged gravel bed and a bag house. Detailed descriptions of both incinerators are available [4].

Kinetics Studies

A series of batch extraction studies investigated the ability of the extractant solution to separate and remove the metals from the ash matrix [5]. Various ash residues were investigated, the Canadian fly ash (CF3) and the Massachusetts fly ash (MF) results will be presented. The extractant solution utilized was 1.0 N NaCl (aqueous), acidified with HCl to achieve an equilibrium pH of 3.0 in the ash-extract slurry. This solution was found to be the most efficient in earlier experimentation [4].

Twenty four HDPE bottles containing 10.0 g ash and 200.0 ml extractant were placed on a rotary shaker and removed at eight different time intervals (in triplicate), up to a steady state period. These intervals were as follows: 10, 20, 30, 45, 90, 180, 300 and 720 minutes. Separation of the solid and liquid phases was carried out through vacuum filtration. The resulting waste extract was analyzed for heavy metals (Pb, Cd, Cr) via atomic absorption spectroscopy, pH, and conductivity.

The kinetics of the leaching process for CF3 and MF ash was investigated through observation of the time dependence of the measured variables. The CF3 extract pH increased from an initial extractant pH of 0.41 to a steady state equilibrium pH of 2.83, while the MF extract pH increased from 1.92 to 2.91 (Figure 1).

The lead extraction curve for CF3 peaked at a reaction time of 10 minutes, and subsequently decreased (Figure 2). Concentration levels in the extract at this time period were

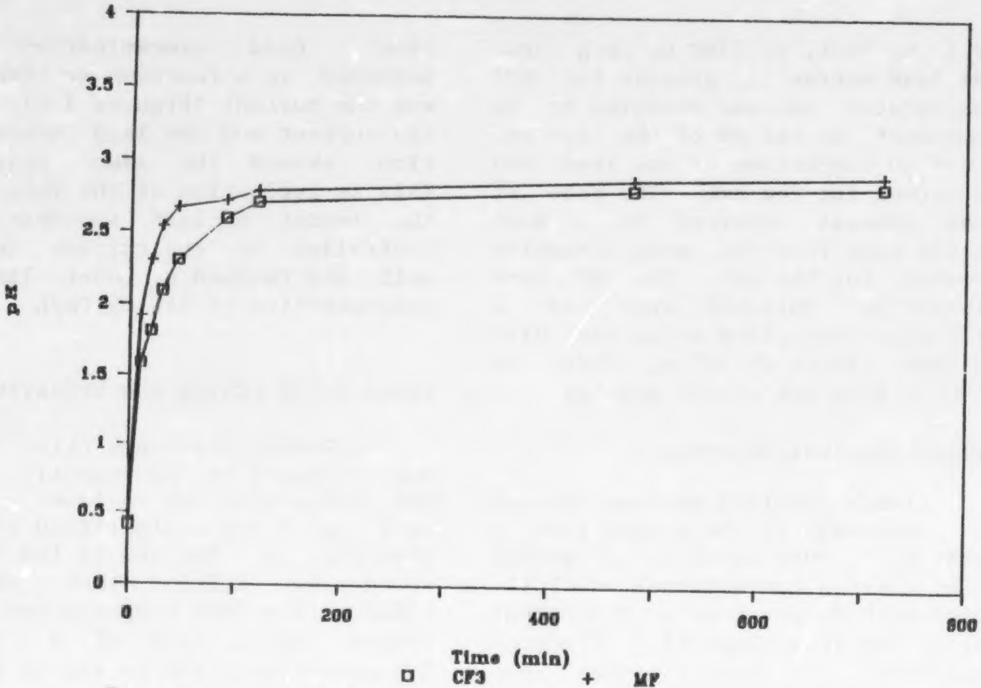

Figure 1 - Batch Kinetics Studies, pH Response in Extract

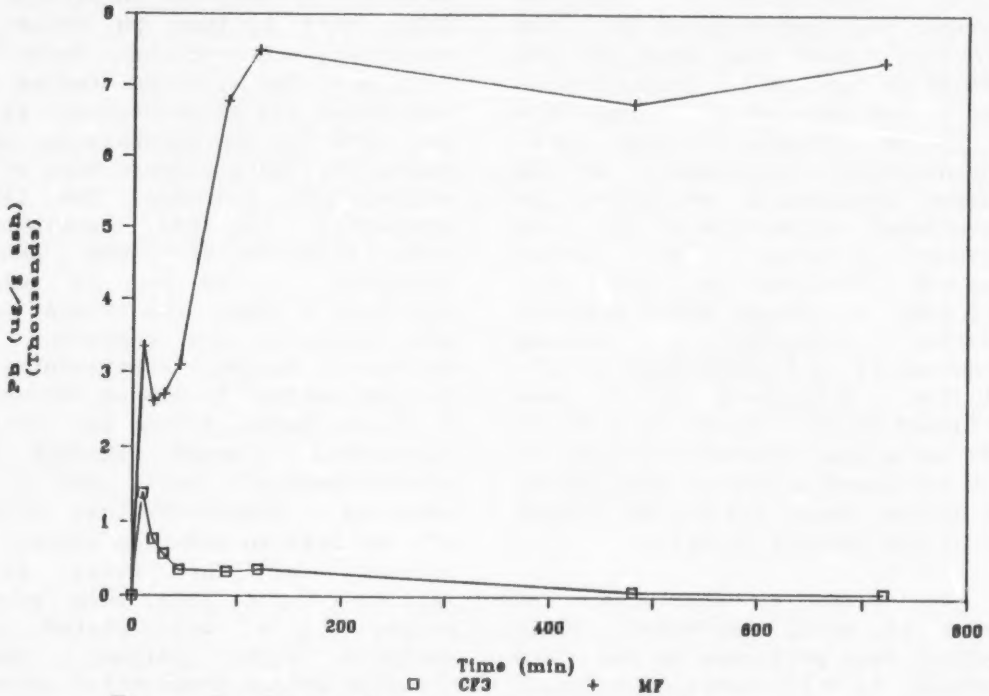

Figure 2 - Batch Kinetics Studies, Pb Response in Extract

69.1 mg Pb/L, or 1380 ug Pb/g ash. The lead extraction process for CF3 incinerator ash was observed to be dependent on the pH of the system, based on comparison of the lead and pH curves for the ash. The rate of lead removal occurred at a much faster rate than the neutralization process for the ash. The MF lead extraction followed more of a diffusion controlled mechanism, with maximum values of 367 mg Pb/L, or 7350 ug Pb/g ash at 720 minutes.

Electrochemical Recovery

Electrochemical methods offered the advantage of the recovery of a relatively pure metal in a usable form; whereas conventional precipitation methods generate a flocculant which requires disposal. Electrodeposition of metals does not require the addition of any extraneous compounds to an already complex solution.

A parallel-plate electrochemical cell was designed for lead recovery. Lead was used as the cathode in this cell. Cyclic voltammetry was carried out using this design on standards of known metal concentration and compared to the aqueous extracts to determine the operational parameters of the lead recovery process. The current response observed in the cell utilizing a 180 mg Pb/L standard solution indicated a plating potential of -0.6 V for lead in this solution. Subsequent cyclic runs performed on CF3 extract at a pH of 3.00 and a lead concentration of 175 mg/L exhibited a peak at this value, indicating that lead may be plated out of the extract solution.

In order to determine the amount of metal recovered, timed studies were performed on the lead standard in a CF3 extractant solution. Lead concentration was measured as a function of time, as was the current (Figures 3,4). Both the current and the lead concentration showed the same response. This is indicative of the fact that the amount of lead recovered was controlled by the current in the cell and reached a lower limiting concentration of 110 mg Pb/L.

PILOT PLANT DESIGN AND OPERATION

A laboratory-scale pilot plant was designed to continuously treat MSW incinerator ash residues; refer to Figure 5 for a simplified process flow diagram. The ash is fed to the continuous stirred tank reactor (CSTR) via a feed hopper/screw pump system at a rate of 1 kg/hr. Extractant solution is fed to to the CSTR at a rate of 20 kg/hr; this flow rate maintains the 1 gram to 20 ml extraction ratio. A pH controller system is utilized to maintain an setpoint pH within the CSTR; this optimum pH value was previously determined from the results of the kinetics studies [5]. The volume and pH maintained within the CSTR are the controlling parameters for the residence time of the solid-liquid reaction. The liquid separation operates continuously with recovery of both phases, utilizing a 20 to 25 micron cellulose filter. The treated solid ash residues are recovered and stored for further experimentation. The ash extract is pumped through a 5 micron basket filter for further filtration, passed through the electrochemical cell and then recycled. Electrochemical plating of the lead in solution allows for recovery of the metal in a relatively pure form; this process occurs in a multi-plated cell equipped with polymer coated titanium anodes (commercial product)

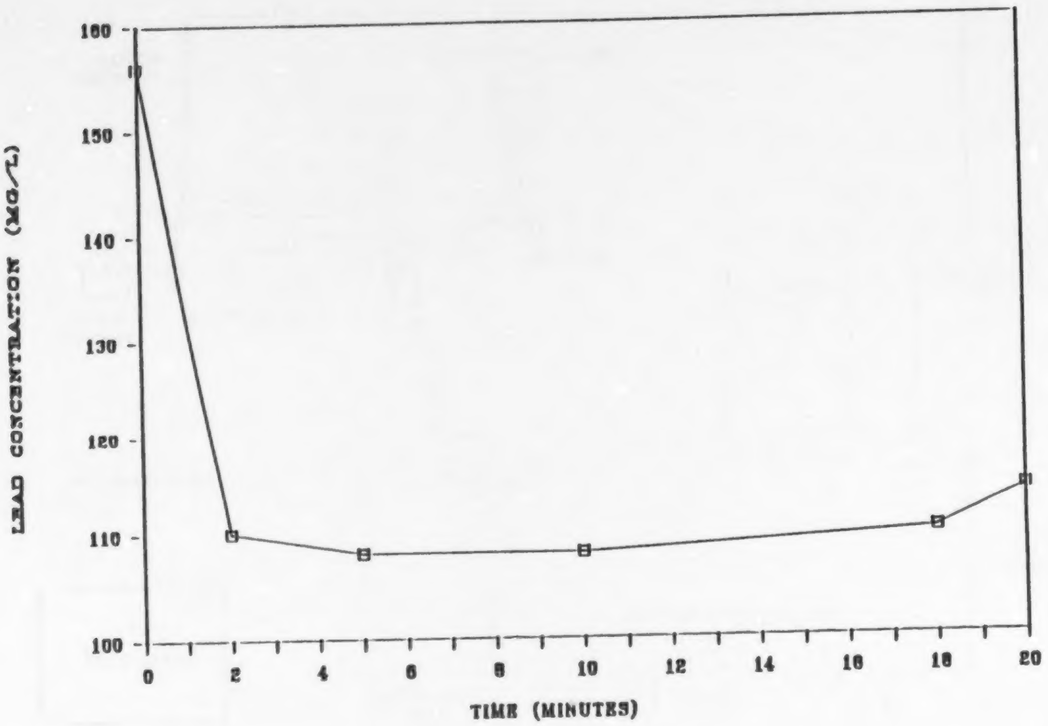

Figure 3 - CF3 Extract Batch Plating, Pb Response

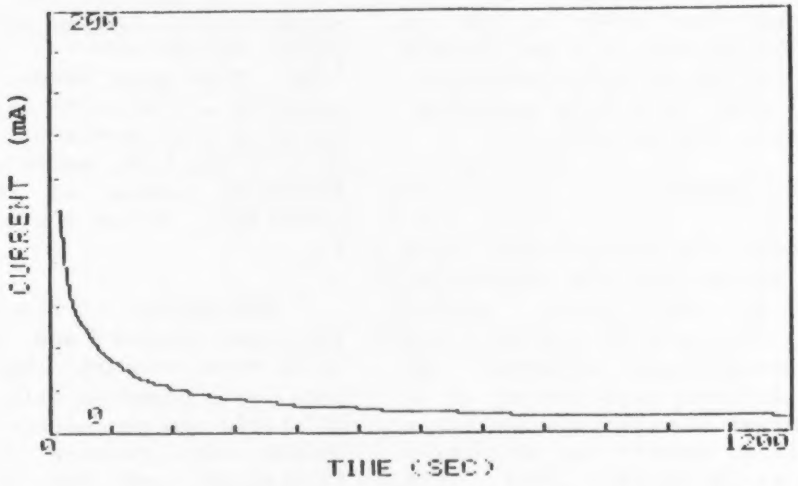

Figure 4 - CF3 Extract Batch Plating, Current Response

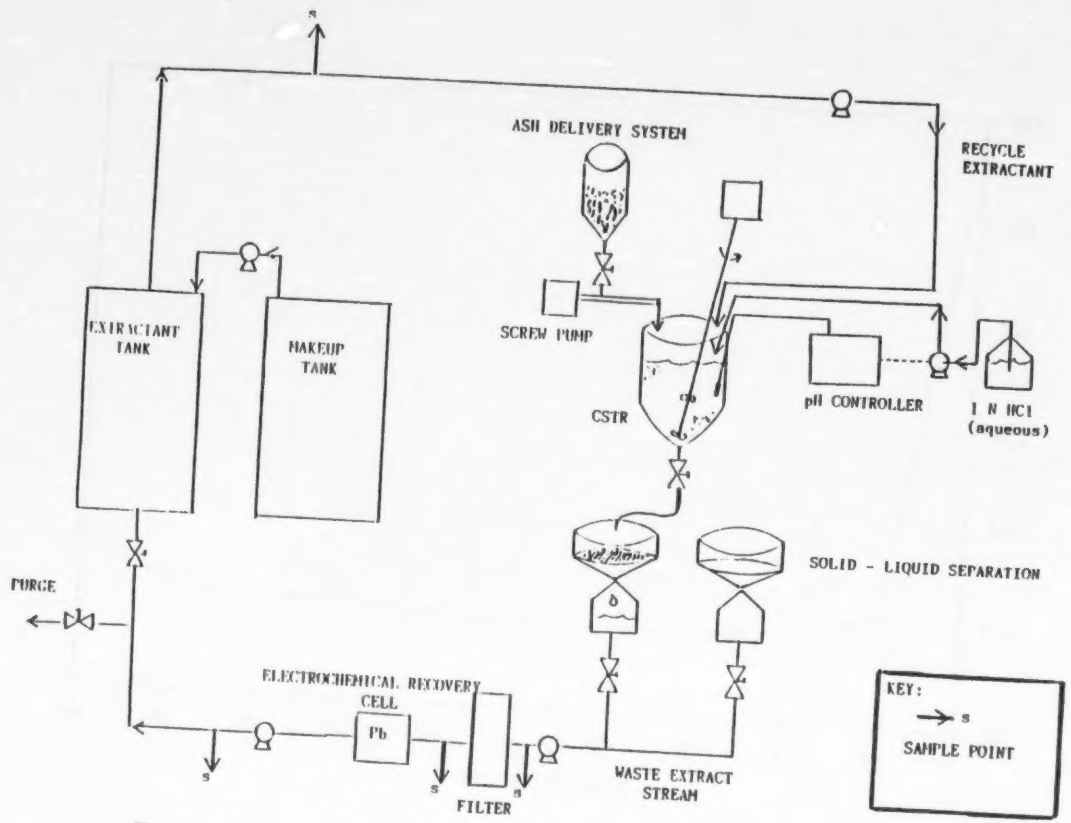
s
ASH DELIVERY SYSTEM
RECYCLE EXTRACTANT
EXTRACTANT TANK
MAKEUP TANK
SCREW PUMP
CSTR
pH CONTROLLER
1 N HCl (aqueous)
SOLID - LIQUID SEPARATION
PURGE
ELECTROCHEMICAL RECOVERY CELL
Pb
s
s
s
FILTER
WASTE EXTRACT STREAM
KEY:
→ s
SAMPLE POINT

Figure 5 - Ash Treatment Pilot Plant Process Flow Diagram

and lead cathodes. The majority of the process equipment in contact with the solid or liquid phases are constructed from HDPE or PVC to avoid interference with the metals analyses as well as avoid corrosion. All pilot plant processes were operated at room temperature.

Extraction Process

Initial investigations were carried out to test the extraction portion of the pilot plant, excluding the recycle stream. The CF3 incinerator ash residues were utilized in these experiments. The pH controller setpoint was set at a pH of 1.59 to control the extraction reaction at the optimum level. This optimal level occurs at the peak of lead extraction from the ash (refer to Figures 1 and 2 for pH and lead concentration curves). The pilot plant was operated for 2 hours and waste extract samples were obtained prior to the electrochemical portion. Subsequent atomic absorption analyses of the waste extract stream revealed high levels of extractable lead in solution, matching the concentration levels at the optimum conditions in batch studies (Table 1).

Subsamples of the treated CF3 ash were obtained and assayed for total metal content. One gram aquilots were digested with 20 ml each of nitric and perchloric acids [6]. Solids were removed using vacuum filtration, and the filtrate was quantitatively diluted to 100 ml and analyzed for metal species; results

Table 1. CF3 Continuous Extraction

Metal	Extract Conc. (mg/L)	Time (minutes)
Pb	43.6	0
	69.2	30
	54.8	45
	158.8	60
	96.2	65
Cd	2.	0
	2.	30
	2.	45
	16.	60
	10.	65
Cr	< 1	0
	< 1	30
	< 1	45
	< 1	60
	< 1	65

are presented in Table 2 and compared to untreated CF3 ash assays. The total lead content decreased from 5750 ug/g ash to 3070 ug/g ash, resulting in a 47% removal of lead from the ash matrix. These results exhibited a 90% decrease for cadmium. Other metals species were not affected by the extraction process; variances observed in the data were due to the heterogeneous nature of the ash solids.

Initial pilot plant experimentation also utilized MF ash to observe the continuous extraction process. The pH controller setpoint was set at a pH of 2.65 to control the extraction reaction at 45 minutes (Figures 1 and 2). The continuous extraction process was carried out for 2 hours, and the extract contained an average of 168 mg Pb/L, correlating to the results from the kinetics studies. The total metal content of the treated MF ash was compared to the untreated ash residues, refer to Table 3. The total lead content decreased from 9150 ug/g ash to 4460 ug/g ash, resulting in a 51% removal of lead. The total cadmium in the MF ash matrix decreased by 81%, and the total zinc content decreased by 56%.

Table 2. CF3 Total Metal Assay (ug/g ash)

Metal	Before Extraction	After Extraction
Cd	210	20
Cr	470	470
Cu	520	610
Ni	74	110
Pb	5750	3070

Table 3. MF Total Metal Assay (ug/g ash)

Metal	Before Extraction	After Extraction
Cd	260	49
Cr	350	170
Cu	740	680
Ni	190	170
Pb	9150	4460
Zn	18300	7980

Electrochemical Process

Batch lead plating experiments were carried out with the pilot plant electrochemical cell and utilized an ash extract solution spiked with a lead standard to a known concentration. The waste extract was obtained through extractions using a fly ash obtained from another incinerator, Massachusetts fly ash (MF). The MF extract was spiked with lead standard solutions to a concentration of 243.0 mg Pb/L. The cell voltage was set at 0.6 V, and after five minutes the concentration decreased to 197.0 mg Pb/L, indicating that lead plating is achievable. Further experimentation will investigate the continuous plating process. Higher lead reductions are expected due to an increased plating time (the cell residence time is 12 minutes) and increased lead concentrations in the extract resulting from the recycle stream.

CONCLUSIONS

The residual ashes from MSW incineration contain high levels of hazardous metals, and leachable concentrations of these materials often surpass the EP Tox test limits as mandated by the USEPA. The classification of these materials may be considered hazardous, warranting costly landfilling. This led to the investigation of the extraction and recovery of Pb, Cd, Cr from the residual ashes. A series of kinetics experiments were carried out, developing the characteristic extraction trends of the various ashes. The extraction kinetics of CF3 ash exhibited a peak in the lead concentration curve at an unsteady state time period of 10 minutes, indicating that the ash/extractant reaction should be controlled at these conditions in order to remove a maximum quantity of lead. Electrochemical experimentation exhibited the potential for metals recovery in a relatively pure form through plating techniques.

Based on the results of these investigations a pilot plant was designed and constructed. Initial experimentation indicated that the extraction process was capable of controlling the extraction reaction at the optimum setpoint. Total metals analyses performed on the treated and untreated CF3 ashes reveal a 47% reduction for lead and a 90% reduction for cadmium. The total lead content in the MF ash matrix was reduced by 51%, while total cadmium and zinc content was reduced by 81% and 56%, respectively. The electrochemical cell plated lead out of solution at a voltage of 0.6 V, and higher lead reductions are expected from increased plating time (the cell residence time is 12 minutes) and increased lead concentrations in the waste extract during recycle operation.

Future experimentation will include the treatment of various other ash residues as well as process optimization to maximize lead and cadmium recovery, including extract recycle. Treated ash residues will be analyzed for leachable metals by EP Tox and TCLP. The design and economic analysis of a full scale ash treatment plant will be investigated, also.

ACKNOWLEDGMENT

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GOVERNMENT-PROVIDED TECHNICAL ASSISTANCE FOR HAZARDOUS WASTE MINIMIZATION

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ABSTRACT

Waste minimization, particularly source reduction and recycling, provides generators the mechanisms to reduce their hazardous waste generation, reduce their waste management costs, and reduce long-term liability. Nonetheless, many businesses remain unaware of the opportunities for waste minimization.

Governmental technical assistance programs have proven to be cost effective methods for encouraging industry to minimize the generation of hazardous waste. The California Department of Health Services (DHS) and local environmental health programs have assisted generators in measurable reductions of hazardous wastes. The most notable is the Ventura County program that achieved a 70% reduction county-wide in the volume of land disposed hazardous waste over a two-year period.

The Department also works closely with EPA through a three-year cooperative agreement to provide waste minimization technical assistance to and funding for generators. This cooperative effort encouraging waste minimization is continuing through the Waste Reduction Innovative Technology Evaluation (WRITE) Program.

Federal, state, and local programs operate in unison. The federal and state programs offer technical materials and financial support to local programs which act as the principal generator contacts. These efforts demonstrate that technical assistance programs can be successful within a regulatory program.

The Department and EPA act as an information and technology clearinghouse. The activities include: publishing "user friendly" waste minimization manuals and fact sheets for generators to evaluate waste minimization options; sponsoring waste minimization training seminars for industry and local government regulators; operating a waste exchange; offering technology development grants to hazardous waste generators; and maintaining a directory of financial resources for waste minimization projects.

INTRODUCTION

Hazardous Waste Minimization -- What is it?

Hazardous waste minimization reduces or eliminates the use of hazardous materials and the generation of hazardous wastes resulting from the manufacture, processing, and use of materials. The overall goal is to eliminate disposal of untreated hazardous wastes to air, land or water. Waste minimization strategies in order of preference include: (1) source reduction: elimination or reduction of waste at the source, usually within a manufacturing process; (2) recycling: the use or reuse of a waste material as an effective substitute for a commercial product or as an ingredient or feedstock in an industrial process; and (3) treatment: a process which eliminates or reduces the hazardous nature of the waste.

Hazardous Waste Minimization -- Why do it?

The regulatory element driving hazardous waste generators toward minimization is the federal and state land disposal restrictions, or Land Disposal Bans. California's Land Disposal Restriction Program has been phasing out the disposal of specific hazardous wastes since 1983. The 1984 Hazardous and Solid Waste Amendments (HSWA) of RCRA prohibit the continued land disposal of about 400 chemicals and hazardous wastes by May 8, 1990. Although treatment technology research and development efforts reduced the volume and toxicity of hazardous wastes, treatment alone will not solve all of the problems associated with the generation of wastes.

Hazardous waste generators should consider implementing waste minimization, such as source reduction or recycling, to reduce the generation of hazardous wastes and costs related to the storage, transportation, treatment, disposal, permitting, and taxation. Businesses that invest staff time and money to incorporate waste minimization techniques will most likely decrease the generation of hazardous wastes, improve the working environment, and be in regulatory compliance.

Hazardous Waste Minimization Information -- Who has it?

In California DHS is the lead agency for the coordination of waste minimization efforts and implementation of RCRA, CERCLA, and other state-mandated requirements. However, it is not the only state agency responsible for environmental management. Two other State agencies responsible for hazardous wastes and pollution control are the State Water/Regional Water Quality Control Boards and the Air Resources Control Board. These media specific agencies are currently working independently; very little coordinated effort is being made for multi-media hazardous waste reduction.

Similarly, local entities exist as counterparts to the State regulatory agencies. Many county environmental health departments actually conduct the RCRA inspections according to Memoranda of Understanding (MOUs) from DHS. Regional Water Quality Control Boards regulate direct industrial discharges and oversee Publicly Owned Treatment Works (POTWs). POTWs, however, have their own powers and are city-owned or are special districts with their own governing bodies. Under the Air Resources Control Board, local air pollution control districts have jurisdiction over air basins which may cross county boundaries. These local entities are autonomous and are in charge of the local regulation of stationary air pollution sources.

Most of the state and local agencies pursuing waste minimization are currently doing so apart from other programs regulating a different environmental medium. There is a serious need to address the fragmentation and lack of communication that characterizes these local efforts through strategies such as formal MOUs, informal agreements, integrated inspections, and other cooperative agreements.

C. PURPOSE

The purpose of this paper is to provide information on federal, state, county, and city sponsored waste minimization programs in California. Projects include (1) EPA's Waste Reduction Innovative Technology Evaluation (WRITE) Program, (2) California's Hazardous Waste Reduction Program, and (3) San Diego and Ventura County's Waste Minimization Programs, (4) City of Los Angeles' Waste Minimization Training Program, (5) California Conference of Directors of Environmental Health, and (6) the Local Government Commission's Guidelines for Hazardous Waste Minimization. All of the following projects received complete or partial funding from the State of California or the U.S. EPA.

D. APPROACH and RESULTS

Waste Reduction Innovative Technology Evaluation (WRITE) Program

The EPA's Waste Minimization Branch and DHS have introduced the WRITE Program to promote preferred waste minimization options for multi-media pollution prevention. This program will evaluate technical and economical aspects of innovative and operational technologies that reduce the volume and/or toxicity of hazardous wastes via source reduction and recycling. The results of the individual evaluations will be consolidated into a state-of-the-art review and be distributed at the state and national level.

The EPA is also sponsoring a national symposium to present industry's waste reduction results. This symposium, scheduled for June, 1990, will provide a national forum to discuss and promote waste reduction, encourage the use of successful innovative technologies, and acknowledge the participating companies and their efforts to reduce the generation of hazardous wastes.

California's Hazardous Waste Reduction Program

The Hazardous Waste Reduction Program is managed by the DHS' Toxic Substances Control Division's Alternative Technology Section (ATS). Specific units within ATS provide the basis for implementing waste reduction and recycling strategies in California. The Waste Reduction Unit manages the state's Hazardous Waste Reduction Grants Program and the Waste Reduction Audit Program. These two programs emphasize technology and information transfer to the hazardous waste generators and the waste management community.

The Resource Recovery Unit focuses on promoting recycling and resource recovery and operates the California Waste Exchange, which publishes the "Directory of Industrial Recyclers" and the "Newsletter/Catalog." The Technology Clearinghouse Unit acts as a focal point for the dissemination of current information on the successes of source reduction and the performance of recycling and treatment technologies. The unit sponsors technology transfer activities such as seminars and classes, as well as, writing and distributing guidelines and fact sheets. The unit's goal is to translate technical literature and information into publications and presentations directed toward specific industries, focusing on small and medium sized businesses.

In February, 1989, a State Hazardous Waste Reduction Award Program acknowledging those companies with operational innovative hazardous waste reduction technologies was started. Based on criteria related to type of industry and waste, technology, status of development, and application to other industries, the best of these will be publicly recognized state-wide and a report prepared for interested parties. This program is being done in tandem with EPA's WRITE Program. Those technologies meeting the criteria of the WRITE Program were further evaluated. The results will be available in a report and presented at EPA's WRITE national symposium.

Ventura County Hazardous Waste Minimization Program

In 1987, Ventura County's Environmental Health Department established a hazardous waste minimization technical assistance program to aid industry in reducing dependency on land disposal. The program identified the hazardous wastes generated in the county in order to prioritize waste reduction efforts, provide waste reduction consulting services for generators, and assist companies in the development and implementation of waste minimization programs which included source reduction, recycling, and on-site treatment.

The waste minimization program was established and strongly supported by the County Board of Supervisors. A "model plan", entitled "Hazardous Waste Reduction Guidelines For Environmental Health Programs", demonstrated that a local government can directly promote waste reduction without hindering established hazardous waste program regulations. The guidelines offer a variety of waste minimization components that can be developed in conjunction with new and expanded hazardous materials program. One of the more notable results is a 70 % volume reduction of hazardous waste being land disposed after 2 years.

To further encourage industry to use waste reduction techniques, a second report, "Ventura County Environmental Health Hazardous Waste Minimization Program Results and Case Studies" was completed. This report summarizes the methodology used by the Program and describes what 55 companies did to reduce their waste generation.

San Diego County's "Promote Landfill Alternatives Now" (PLAN)

San Diego County's Department of Health Services developed a comprehensive hazardous waste minimization program entitled "Promote Landfill Alternatives Now!" (PLAN). Various strategies were developed to promote waste minimization and assist businesses with implementing modifications. The PLAN also served as a focal point for the community to voice concerns pertaining to hazardous waste management, thereby enhancing the level of communication between government agencies, industry, and the public.

Results of this program are the development of industry-specific questionnaires, workshops, and booklets which summarize waste reduction techniques. Another was to train county staff how to conduct industrial waste minimization audits and how to incorporate the audits as part of compliance inspections. Third, a computer file was designed to compile data from waste minimization audits, local waste information, and waste stream-specific pollution control alternatives. Lastly, a graduate work-study program with a university engineering department emphasizing waste minimization was established to assist industries.

City of Los Angeles Waste Minimization Program

The City of Los Angeles has established a Hazardous and Toxic Materials Project to ensure that City Departments and industries promote and practice hazardous waste minimization. The program promotes source reduction and recycling of hazardous wastes to reduce discharges to air, water, and land. One potential result of this program is the reduction of heavy metals and other toxic wastes being discharged to the City sewer system, as well as the disposal in off-site landfills.

Waste minimization technical assistance is also being provided to industries through the City's Bureau of Sanitation. This was accomplished by first offering training to city industrial waste inspectors and sanitary engineers, as well as industry personnel. The training increases the level of awareness of waste minimization and hazardous waste requirements so that information can be transferred to industry personnel during routine visits. Practical methods are also being developed for inspectors and industry to determine if a waste minimization program was in fact reducing the overall generation of hazardous wastes without transferring undesirable components of the wastestream to a different medium.

These waste minimization methods are being evaluated at 10 to 20 electroplating companies using cadmium, nickel, lead or chromium in their process. Technical assistance is being provided by City staff and an engineering consultant to generators to determine the efficacy of the methods and the extent of waste minimization. A final report detailing the results is expected in May, 1990.

Local Government Commission

The Local Government Commission of Sacramento (a non-profit, non-partisan membership organization of elected and appointed officials) has produced three guidebooks designed to help local governments establish waste minimization programs.

Low Cost Ways to Promote Hazardous Waste Minimization: A Resource Guide for Local Governments.

This guidebook describes why and how local governments can set up educational, technical assistance, and regulatory outreach programs for hazardous waste minimization. A complete resource listing for 28 low cost activities are provided in detail. The guidebook also provides examples of successful local government programs. A model resolution for establishing an educational program to assist businesses in the cities and counties is also included.

Reducing Industrial Toxic Wastes and Discharges: The Role of POTWs.

This guidebook explains the importance of Publicly Owned Treatment Works (POTWs) and the opportunities for promoting hazardous waste minimization. POTWs can help area firms significantly reduce their toxic discharges to the sewer, without transferring those same pollutants to other media, by developing educational, technical assistance, and regulatory programs. A model POTW resolution for developing a hazardous waste minimization program, examples of established programs, and appendices with useful information are included.

Minimizing Hazardous Wastes: Regulatory Options for Local Governments.

This guidebook describes the program and regulatory framework that can be used to promote multi-media, multi-agency hazardous waste minimization at the local level in California. It explores and identifies the role of direct requirements, indirect regulatory inducements, and positive incentives for waste minimization. A model resolution for developing a hazardous waste minimization program at the local level and appendices of related information are included.

California Council of Directors of Environmental Health

The needs and concerns of local environmental health programs are represented by an organization entitled the California Conference of Directors of Environmental Health (CCDEH). CCDEH meets regularly to address policy issues, develop positions on proposed legislation, and provide a forum for discussing consistency in enforcement of California's laws and regulations.

CCDEH recognizes the utility of developing strong and effective waste reduction programs and has established a subcommittee of individuals who are active in this area. The CCDEH Waste Reduction Subcommittee meets every two months to discuss the latest developments in waste reduction, resolve problems associated with implementing waste reduction programs at the local level, and to exchange information between local programs in order to avoid duplication of efforts.

A current goal of the Subcommittee is to assist counties without waste reduction programs and provide them with the information, tools, and support to develop effective programs. The Subcommittee, in conjunction with the Department's Technology Clearinghouse Program, is currently developing two one-day training sessions on the basic concepts of waste reduction as it relates to local enforcement efforts. The ultimate goal of the Subcommittee is to provide all counties with information on how to effectively implement waste reduction.

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

ROTARY KILN INCINERATION SYSTEMS: OPERATING TECHNIQUES FOR IMPROVED PERFORMANCE

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ABSTRACT

Experience in the operation of rotary kilns goes back many years with the thousands of kilns throughout the world. However, much of this experience is in the cement, lime, and calcined dolomite industries. In the past twenty to thirty years, rotary kilns have been used in the incineration of municipal and industrial wastes. The operating practices differ in that the industrial kilns are used to generate a quality-controlled product. Flame size and shape, heat transfer by radiation and convection, temperature distribution, and contact-time all play a critical part in the quality of the end product. These kilns are normally 50 to 200 meters (150 to 600 ft.) in length.

Kilns used for incineration are typically batch fed with solids of varying shape, size, and heat content. This provides flexibility not available in other incinerator systems. These kilns may also burn liquids, slurries, sludges and contaminated soils at a continuous feed-rate. The Resource Conservation and Recovery Act (RCRA) establishes the combustion performance required to obtain an operating permit. Many existing kilns have been modified in design and operating practices to allow the system to meet RCRA standards. These modifications have included feed devices, seals, lance design and location, controls, scrubber systems, monitors, safeties, etc.

This paper covers the experience gained at several rotary kiln installations burning hazardous wastes. This includes the modifications in design and operation to minimize fugitive emissions, temperature, pressure and stack emission upsets. This has provided systems whose performance insures a safe environment to the owner and the surrounding community.

INTRODUCTION

Early development of the rotary kiln started about 1877 in England. The first commercial rotary kiln was the result of the proven work of American engineers in 1895, by Hurry and Seaman of the Atlas Cement Co. Those first kilns were 45 cm (18 in) in diameter and 4.5 meters (15 ft) in length. Kiln sizes started to explode in the 1960's when they reached dimensions up to 6.5 meters (21 ft.) diameter and up to 238 m (780 ft) in length.

The energy crisis of the 70's represented a blessing in disguise in matters of kiln design. This occured world wide when modifications to preheaters were made along with use of alternate fuels. The major breakthrough came in Europe where precalcination was successfully attempted in the late 1960's using a very low BTU bituminous shale as a component of the kiln feed. As early as 1957, oil shale in slurry form was used as a potential source of energy in Canada (4).

Other wastes burned in cement kilns have included brines, aqueous metal-bearing wastes, acidic wastes, lime-alum sludges, halogenated wastes, spent solvents and still bottoms (2).

Although cement kilns will accommodate a variety of materials both as fuel and feed in the cement process, there are limitations in the use of hazardous wastes as there are compounds not desirable in the cement process. The experience gained in this industry has led to the acceptance of the rotary kiln as a means of disposing wastes, both hazardous and non-hazardous by incineration.

Rotary kilns provide a number of functions necessary for incineration. They provide the conveyance and mixing of solids, a mechanism for heat exchange, serve as a host vessel for chemical reactions and provide a means of ducting the volatilized gases for further processing. The kilns are equally applicable to solids, sludges, and slurries and are capable of receiving and processing liquids and solids simultaneously (7).

WASTE DATA

Waste streams in the process industries are numerous in kind and therefore defy easy definition. Disposal of these wastes has become a serious problem for the plant operator. The following waste data must be provided before a selection of incinerator design can be completed.

Waste Data Required for Design

Chemical Composition
Specific gravity
Heat of Combustion
Corrosivity
Ignitability
Reactivity
Moisture Content
Size Consistency
Slagging properties
(Temp., Eutectic Data)

The quantity of the waste materials in total; that is, solids, sludge, slurries, liquids (and fumes), will determine not only the total throughput in units of weight (tons, kg, pounds) per unit of time (min, hr, day, year), but also the total heat duty requirements of the systems.

INCINERATOR TYPES

The physical data will aid in determination of the type of incinerator designs that can be considered. There are many types that may be used to incinerate hazardous wastes. They are as follows:

Liquid Injection Incinerators
Rotary Kiln
Fixed Hearth (Two-Stage)
Mono-Hearth (Rotating)
Multiple Hearth
Fluidized Bed
Infra-Red Furnace
Rotary Reactor (Cascading Bed)
Molten Glass Process
Wet Oxidation

Many of these designs are limited to a feed that is prepared specifically for the incinerator type, i.e., liquids and slurries that may be pumped and atomized. Others require a limit to the physical dimensions of the feed and require pretreatment; i.e., shredding prior to introduction to the transport system. Some designs will handle only easily transported sludges and soils. The rotary kiln and fixed hearth are ideally suited to large size solid feeds such as bulk trash, containerized process waste solids, as well as contaminated soils, sludges, slurries and liquids. The fixed hearth design requires multiple ram feeders to expose the surface of the waste materials to the combustion and heat exchange process. This paper will highlight the rotary kiln incinerator since it is the most flexible of solids incinerator designs today. Others (fluid bed, rotary reactor, etc.) are used for incinerating solids and require extensive feed preparation and transport to optimize the mixing, heat transfer, and combustion which are considered major advantages for these other designs (Fig. 1).

One major feature of both kiln and fixed hearth designs is that most solid wastes must be batch fed. Other systems can accept wastes continuously into the combustion zone; this provides improved combustion and emission control. This is a singular disadvantage to the operation and performance of batch-fed incinerators. However, experience gained in the past few years driven by the RCRA regulations has minimized this disadvantage. The standards developed by U.S.E.P.A. via RCRA and now implemented by most of the States' Solid Waste Authorities are as follows:

RCRA Standards (5)

1. 99.99% Destruction and Removal Efficiency (DRE) of the Principal Organic Hazardous Constituents (POHC)
2. 99% removal of Hydrogen Chloride (HCl) or HCl emission not exceeding 1.8 Kg/hr (4 lb/hr)
3. Particulate emission concentration of 180 mg/dscm (0.08 gr/dscf) corrected to 7% O_2.

Guidelines have been issued

Guidelines have been issued to permit regulators to insure that these standards are being met during the trial burns and subsequent operation of the system. These apply to the carbon monoxide emission monitoring which is the surrogate used to establish conformance to the 99.99% DRE. Guidelines are also in final stages regarding the metals emissions issues. Standards covering particulate emissions may be lowered to 0.015-0.02 gr/dscf to insure metals emission control. Many states have established maximum emission levels well below the 0.08 gr/dscf. These levels are based on the "Best Available Control Technology" (BACT) demonstrated at operating facilities within the state.

ROTARY KILN OPERATIONS PAST AND PRESENT

In order to conform to the above standards, past operating practices at many rotary kiln incinerator facilities have had to be modified. Many incinerator systems under "Interim Status" (Part "A" permit) have been operating with the following conditions as normal practice.

Past Practices

1. Batch Feed System:
    - Manual (Under operator control)
    - Cycle for load (Varied from 15 to 30 min.)
2. Kiln Draft Pressure:
    - Manual (Under operator control)
    - Positive pressures created fugitive emissions.
3. Combustion:
    - Air/fuel control (Under operator control)
    - Auxiliary fuel (Manual)
    - Afterburner (Volume undersized)
    - Temperature Control (Manual)
    - Burner (Design or Location)
    - Atomizer (Design or Location)
4. Scrubbers:
    - Submicron particulate efficiency (Poor)
    - PH control (Manual)
    - Corrosive atmosphere overlooked in material selection.
    - Many systems had no Scrubbers.

These operating conditions resulted in stack emissions of odors and particulate emissions in the surrounding community. The term "NIMBY" (Not in My Backyard) was originated. The environmental groups soon formed to block any future installation of incinerator systems.

Those facilities operated as on-site (industrial plants) or off-site (commercial disposal operators) have made many changes and improvements to comply with RCRA requirements. As stated above, most of these were driven by the modifications needed to complete the Part "B" permit and the final trial burn at the facility. At most plants preliminary test burns were run to determine existing capabilities. These tests (mini-burns) resulted in many or all of the following design and operating improvements. This allowed the system to meet the final standards for the trial burn (6).

Improvements

1. Feed System

   - Continous Feed:
     - Shredder
     - Lump and Cake Breakers
     - Weigh Belt Control
   - Feed Devices:
     - Auger
     - Screw Feed (Single and Multiple Screws)
     - Belt Feeder
     - Elevator
     - Ram
   - Batch Feed:
     - Container Size Control
       - Volume
       - Weight
     - Container BTU Control
     - Cycle Time Modifications
     - Bar Code for Control
   - Mechanical Improvements: (Fig. 2)
     - Roller Conveyors
     - Elevators
     - Intermittent Ram Feeder
     - Holding Chamber
     - Guillotine Door Size Reduction

2. Combustion System (Fig.3)

   - Combustion Air Control
   - Improved Seal Design
   - Air Flow Meters to Primary/Secondary
   - Oxygen Monitoring at Secondary Level
   - Auxiliary fuel burner type/location
   - Heat input control by waste types
   - Secondary Combustion Chamber Design/Mixing
   - Atomizer Design Modifications/Locations
   - Temperature Monitors/ Number/Location
   - Maximum Temperature Control Via Air/Water

3. Pollution Control System (Fig.4)

   - Combustion Chamber Design
     - Control velocity and carryover
     - Orientation to prevent ash-buildup
   - Waste Injectors
     - Location and size to minimize attrition
   - Ash System
     - Hopper size/bridging
     - Temperature control slagging or freezing
   - Quench Design
     - Quench liquid control
     - Temperature of operation
   - Scrubber
     - Venturi Throat
     - Control materials of construction
   - Absorber
     - Packing
     - Demisters
     - pH control

CASE STUDIES

Experience with retrofit and modifications to liquid injection incinerators has been covered in detail. Many changes were required in order to obtain approval for the Part "B" permit (6). As stated above, former practices with solids incinerators led to problems which generated excessive emissions of particulates as well as products of incomplete combustion (PICS). Solid waste materials are often collected in 55 gallon drums to minimize handling and labor costs. These drums vary in weight from 400 pounds to as high as 900 pounds depending on the density of the materials. The physical size of the drum establishes the feed mechanism size; i.e., belt, chute feeder, elevator, ram feeder, and guillotine door. This establishes the kiln opening. The kiln inside diameter is then established. The two limits to kiln capacity are as follows:

1. The maximum feed rate of solids in pounds per hour.
2. Maximum heat release rate in BTU per hour.

Both must be evaluated to determine whether an existing kiln is operating at its optimum conditions. Combustion systems are optimized when operated at a steady feed rate with a uniform heating value of feed with a combustion air rate that maintains constant oxygen level in the stack gases. Process furnaces or boilers operate at maximum efficiency; i.e., at minimum excess air (O_2). Waste burning systems do not run with low excess air levels (1-3% O_2). Most liquid waste incinerators operate with stack at 3 - 5% O_2. This insures against variations of waste composition and heating value. When burning solids, waste rates and BTU values are even more difficult to control. However, it is possible to operate with proper air controls at levels of 6 - 9% O_2 continuously.

Many existing kilns have poor seal designs. This will result in high excess air drawn into both front and rear seals during operation. Some systems have experienced excess air levels of 100 to 150%. A major disadvantage created by the poor seal problem was limiting the heat release of the kiln. The high velocity created by this additional volume causes fine particle entrainment into downstream equipment. This volume adds to the heat load of the afterburner. Residence time in the afterburner must be held in order to meet RCRA standards. The gas volume establishes the physical size of the downstream air pollution control system and induced draft fan.

Air in-leakage also occurs at the feed chutes and guillotine doors. Reduced leakage at these points, decreases the velocity in the kiln and the particulate carryover. However with a fixed heat input, the temperature will increase in the kiln. Combining the same total heat input with additional inert materials such as soils and moisture, the same physical chamber size can be modified to process an increased daily tonnage of materials. The cooling by water addition from the wet feeds or waste water sprays results in a reduction of total gas flow in the kiln. This will minimize kiln gas velocity and carryover. The afterburner design must provide the necessary turbulence and temperature rise needed to provide the 99.99% DRE of the organic components in the waste.

The solid feed rate limits are determined by several factors. The physical dimensions of the kiln (diameter, length and slope) and the rotation (rpm) establish the residence time of solids. This must be reviewed based on the volatility their surface heat absorption rate from the temperature and O_2 in the kiln gases. This heat absorption rate is dependent upon the physical nature of the solids, the water content which establishes the drying load, and the inert materials (ash) in the waste (Fig. 5). For good heat transfer, volatilization and combustion of the organics, a solid volume fraction of 5 to 15 % is recommended. Typical residence time of solids may vary from 30 minutes to 2 hours.

Many kilns were operating at loading rate cycles that varied from 10 minutes to as long as 30 minutes. The resulting variation in kiln pressure and temperature often was out of control of the operator. Puffing at the seals would occur with PICS entering the operating area. The afterburner control also was difficult to maintain. Temperatures would follow the variations created in the kiln. Since the kiln heat release rate would vary, and auxiliary firing of the afterburner was by a forced draft burner, there was no means for controlling stack O_2 levels. The result would be large variations in stack oxygen. After monitors were placed on the stack for carbon monoxide (CO) or total hydrocarbons (THC), large spikes would be observed many times to the upper limit of the scale (3000 - 5000 ppm). At the same time, O_2 would drop to 0%.

The capacity of a system in total heat release rate is established by the volume of combustion air provided in the forced draft (FD) and induced draft (ID) fans. The individual burners are limited by the FD fans. The total incineration system (kiln and after-burner) is limited by the I.D. fan capacity. One must first establish the level of O_2 needed for satifactory operation. Having the I.D. fan data (ACFM @ Temp.), one may calculate the dry SCFM handled by the fan. Based on the oxygen level for the system, the excess air level may be established (Fig.6). The total BTU capacity for the incinerator system may then be determined by the following formula:

BTU/hr =
(DSCFM x 6000)/Total Air
- where -
Total Air =
1 + excess air fraction.

Having established the maximum heat release of the system, one would now review the capacities in both kiln and afterburner. The kiln is the critical zone since it is a batch fed combustor. Certain wastes due to feeding problems and the nature of the waste must be fed continuously; e.g., sludges, slurries and waste water streams. The heat release for these should be relatively stable if proper measures have been taken in the storage and mixing areas. The heat release from the batch fed wastes will be dependent upon the weight per charge, the BTU/charge, and the relative volatility in each charge. If each drum is prepared consistently, the values of weight, BTU, and volatility will be steady. The result is a cycled heat input dependent upon cycle time and the BTU/charge. Locations with the ultimate in control of waste feed have experienced sudden energy release from charges into the kiln. This is followed by a sudden increase in temperature and a rapid decrease of O_2 exiting the chamber. The total volume of air in the kiln is maintained at a fixed rate by the draft created by the I.D. fan. With the rapid depletion of O_2 in the kiln, the stack gas emissions drop in O_2 and increase in CO and THC. If these reach permit shutdown levels, all waste feeds must be cutoff per present regulations. In past operations, continuous monitors such as kiln draft, O_2, CO, etc. were not required and waste cutoffs were manually controlled by the incinerator operator.

In order to minimize these upsets, modifications were made in the operations and controls. In the case of continued spiking due to high volatility (BTU) of the waste feed, the charge size was reduced and fed more often. One incinerator was designed to operate with stack gas containing 10% O_2 average. The original charge of 270 lbs. with a heat content of 1.66 MM BTU was fed every 15 minutes. Note from Fig. 7 the effect of materials volatilizing in three (3) to five (5) minutes. The five minute volatilization would reduce the O_2 to 4.5%. However, with volatilization occuring in three minutes, there was not enough air to operate without high levels of CO and PICS. By reducing the charge size to 90 lbs. (0.55 MM BTU) charged every 5 minutes, the system was able to stay in control with either a 3 minute or 5 minute volatility material (Fig. 8) (6).

By utilizing the oxygen analyzer as a control device, another incinerator system was brought under control reducing waste feed cutoffs. Fibre-packs are fed at a fixed rate with the feed rate based on BTU/ charge (Fig 9). Occasionally, a "hot" drum would enter the kiln. A "hot" drum is one containing free liquids. This resulted in a sudden drop in O_2 measured at the exit of the after-burner. In this case, the kiln steady state firing rate was 30 MM BTU/hr and the afterburner - 70 MM BTU/hr. The total heat release rate from the system averaged 100 MM BTU/hr. Normal operation resulted in waste feed cutoffs two to three times daily. With all of the auxiliary heat added by the waste liquids into the afterburner, a waste feed cutoff resulted in waste solids continuing to burn in the kiln with no additional heat input to the afterburner. The CO level would spike followed by a prolonged time period with high THCs in the stack gases. With the I.D. fan operating at fixed output, the kiln and afterburner chambers would cool rapidly increasing the THC levels.

The first indication of a problem is the dropoff of O_2 level. This is followed by the CO spike. By monitoring the O_2 level (6 to 7%) and using the average - 6.5% as a control point, a dropoff of 1.5% indicates a problem may be in the initial stage. Since the liquid firing rate was 70% of the total heat input, this was used as a control to maintain O_2 level at a fixed afterburner temperature. The initial 1.5% O_2 drop triggered a reduction of liquid heat input by 50%. A continued drop of the O_2 level reduced liquid heat input an additional 30%. This drops the total heat input by the liquid to 24% from the 70% level (70-.8x70).

Most often this would be sufficient to keep the O_2 level from reaching the waste feed cutoff point - 3%. This assumes that the sudden heat input from the kiln feed has increased from a level of 30% to 76% (more than 2.5 times). In many cases. The heat input from the volatile solids would be less with other waste streams entering the kiln such as sludges and slurries at a constant flow and BTU input. This control modification has reduced the number of waste feed cutoffs from O_2 trips with the resultant spikes of CO and THC. These control modifications are needed to insure the environment in the area of the incinerator for the operators as well as that for the surrounding community is maintained. Complaints of odors from the "NIMBY" groups may be justified based on past practices. The modifications needed to improve operating conditions and essentially eliminate these problems are possible. It requires close observation of the daily operating procedures, discussions with the operators and review of the strip charts and log books. Only then can one determine that there are problems and that modification to operating procedures or controls will eliminate the problem. In many cases however, redesign of the basic hardware will be needed to achieve the control necessary (Fig.10).

SUMMARY

The cases described above cover instances where improvements have been made to meet the standards established by RCRA. The results have shown an improvement in the efficiency of the operation as well as lower operating costs. One major benefit has been in lowering maintenance costs, especially in refractory repair. Closer control of heat input has maintained more uniform temperatures which has resulted in increased refractory life. It also reduces downtime and provides higher utilization of the equipment. Additional capital expenditures were necessary to make these modifications. Training costs were also higher. All of this has resulted in operating plants who pride themselves with systems that provide not only increased employment and revenues to the local community, but also a means of eliminating the hazardous materials from the environment forever. It has allowed the rotary kiln to become one of the most flexible incinerator designs for all hazardous waste streams. From its original use as a process furnace, it can now be found in use at MSW plants, commercial hospital waste disposal facilities, and large commercial hazardous waste sites. The design most often selected for many large on-site facilities has been the rotary kiln, either slagging or ashing. Many of the mobile or portable units used for Superfund (SARA) cleanups have been the rotary because of its flexibility in handling the variety of waste types and physical shapes.

Many rotary kiln incineration systems have been modified and tested for the RCRA and TSCA permits in the past 10 years. This testing has shown that rotary kilns can achieve DREs well above 99.99% and often > 6 - 9s. The incineration of hazardous wastes in a rotary kiln has become popular because the designs, concepts, and theories are well established and proven in many solids processing industries. The effort to meet the standards established by RCRA has enabled the latest control and instrumentation technologies to be included in the design and operation of all systems. (1,3,8) It is extremely important that the technical community who understand the results of these improvements inform the citizens who oppose siting of units about the advantages of a properly designed and operated incineration system to effective disposal of hazardous wastes.

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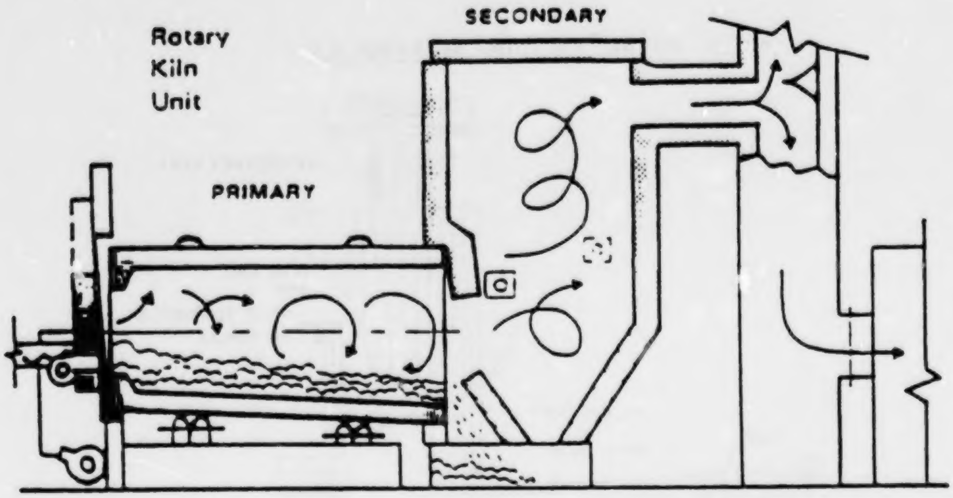
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Kiln
Unit
SECONDARY
PRIMARY

FIG. 1.

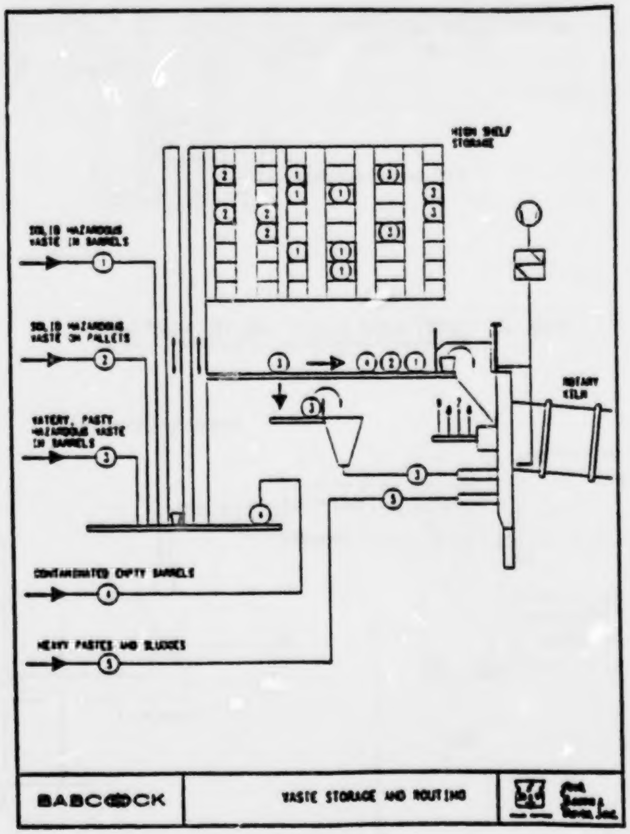

HIGH SHELF STORAGE
SOLID HAZARDOUS WASTE IN BARRELS
SOLID HAZARDOUS WASTE ON PALLETS
WATERY, PASTY HAZARDOUS WASTE IN BARRELS
CONTAMINATED EMPTY BARRELS
HEAVY PASTES AND SLUDGES
ROTARY KILN
BABCOCK
WASTE STORAGE AND ROUTING

FIG. 2.

FIG. 3 ROTARY KILN AND AFTERBURNER

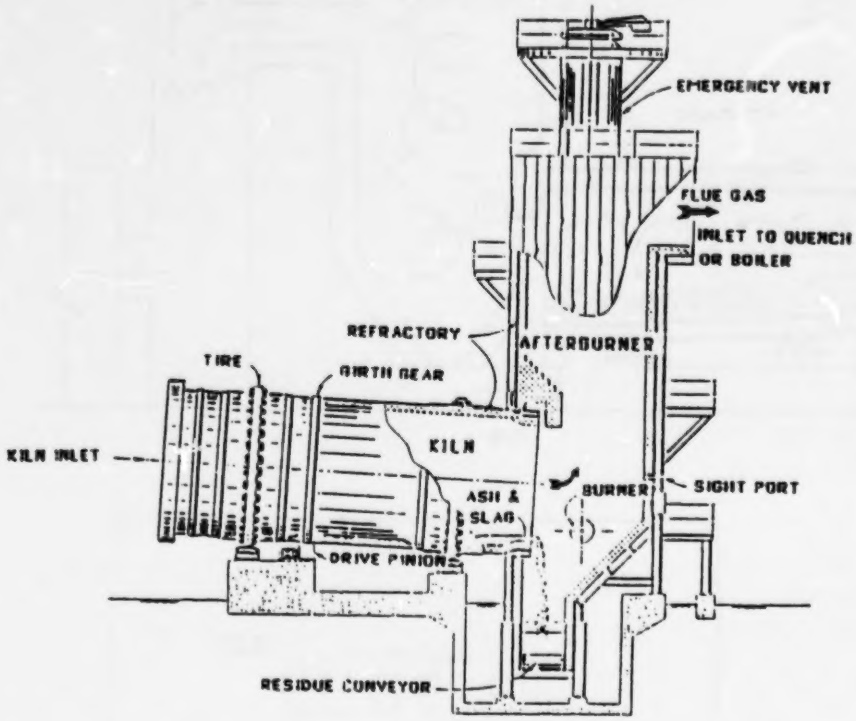
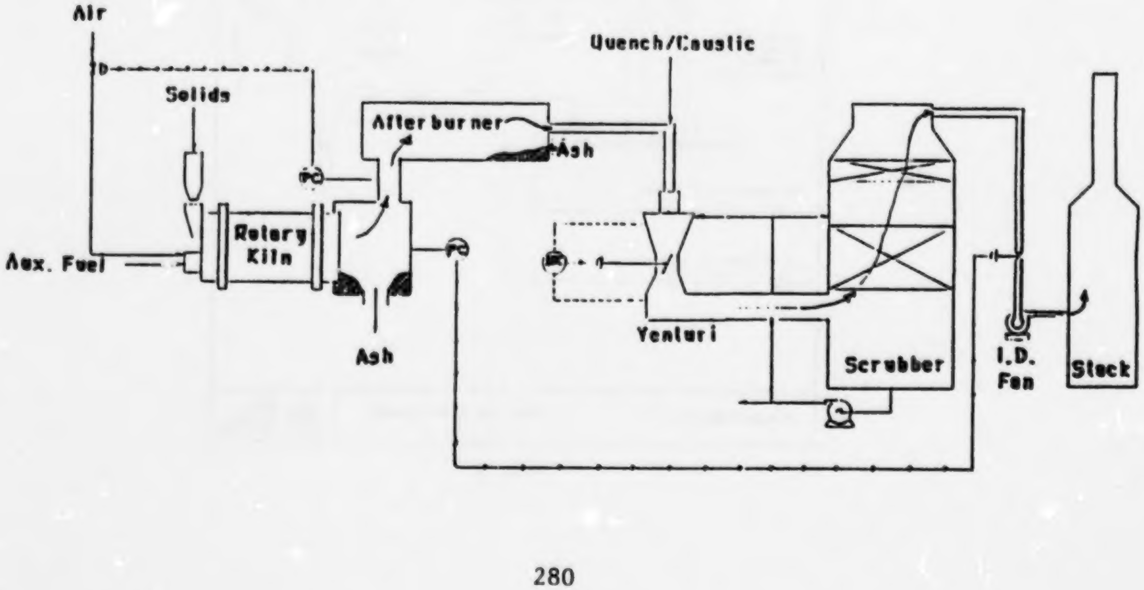

EMERGENCY VENT
FLUE GAS
INLET TO QUENCH OR BOILER
REFRACTORY
AFTERBURNER
TIRE
GIRTH GEAR
KILN INLET
KILN
ASH & SLAG
BURNER
SIGHT PORT
DRIVE PINION
RESIDUE CONVEYOR

FIG. 4. ROTARY KILN INCINERATOR


Air
Solids
Quench/Caustic
After burner
Ash
PC
Rotary Kiln
Aux. Fuel
PC
Ash
Venturi
Scrubber
I.D. Fan
Stack

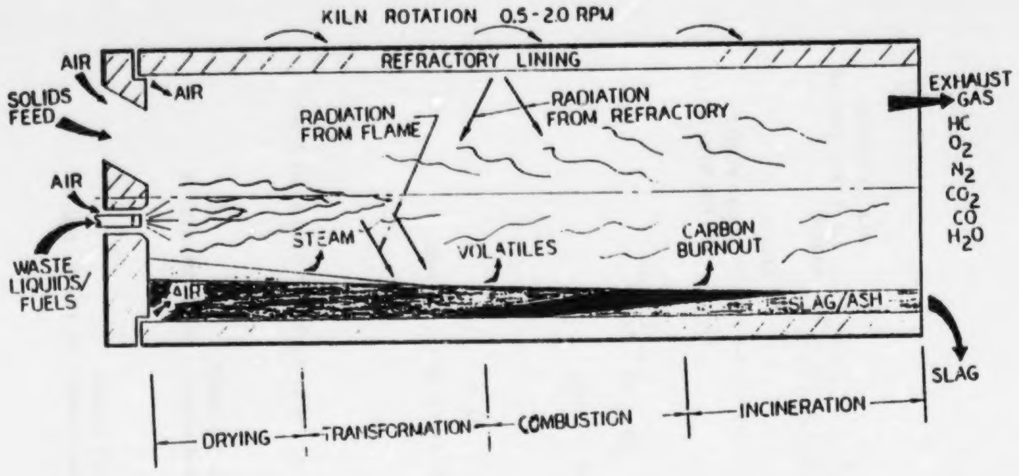

KILN ROTATION 0.5-2.0 RPM
AIR
REFRACTORY LINING
AIR
SOLIDS FEED
RADIATION FROM FLAME
RADIATION FROM REFRACTORY
EXHAUST GAS
HC
O_2
N_2
CO_2
CO
H_2O
AIR
STEAM
VOLATILES
CARBON BURNOUT
WASTE LIQUIDS/ FUELS
AIR
SLAG/ASH
SLAG
DRYING
TRANSFORMATION
COMBUSTION
INCINERATION

FIG. 5. ROTARY KILN PROCESSES

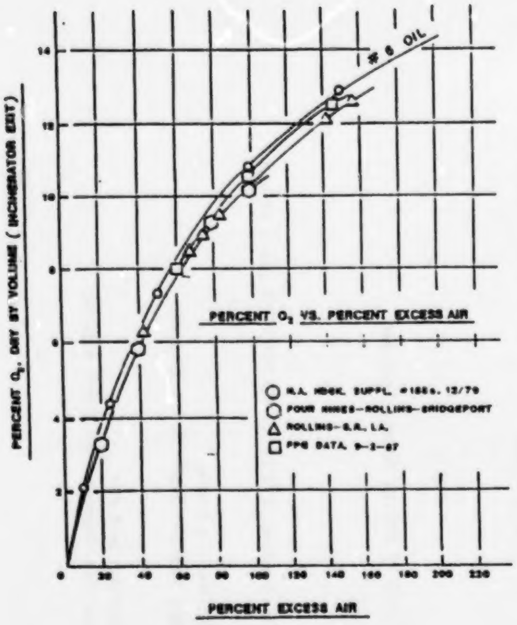


FIG. 6a. ROTARY KILN OPERATING CURVES

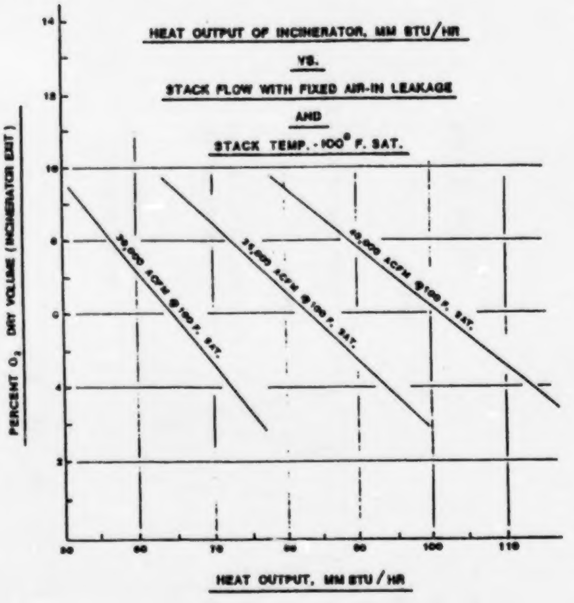


FIG. 6b. ROTARY KILN OPERATING CURVES

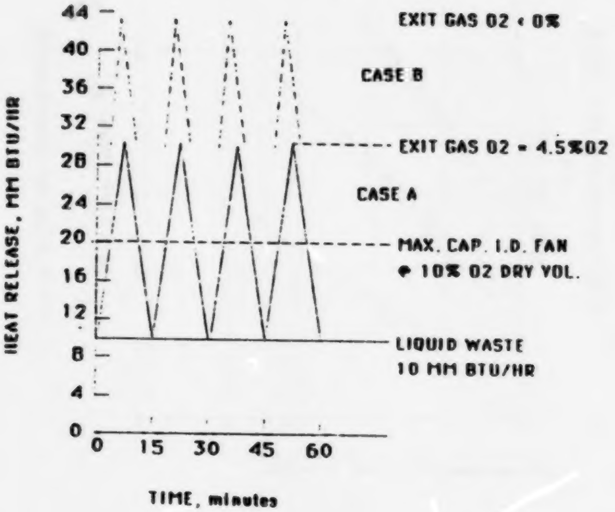


Fig. 7

EFFECT OF SOLIDS VOLATILIZATION

Solids Loading, 270 lb. (1.66 MM BTU) every 15 min.

CASE A   Volatilizes in 5 min.
Equiv. Heat Release - 20 MM BTU/HR

CASE B   Volatilizes in 3 min.
Equiv. Heat Release - 33.2 MM BTU/HR

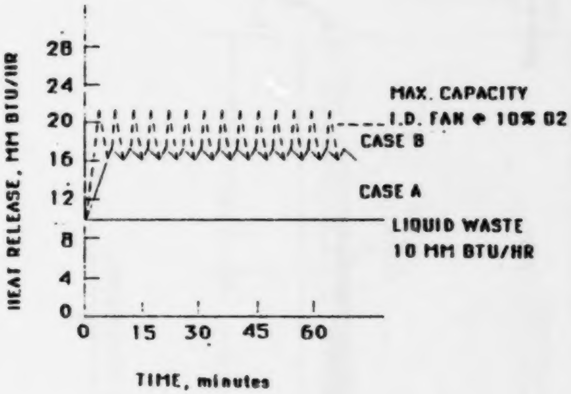


Fig. 8

EFFECT OF SOLIDS VOLATILIZATION

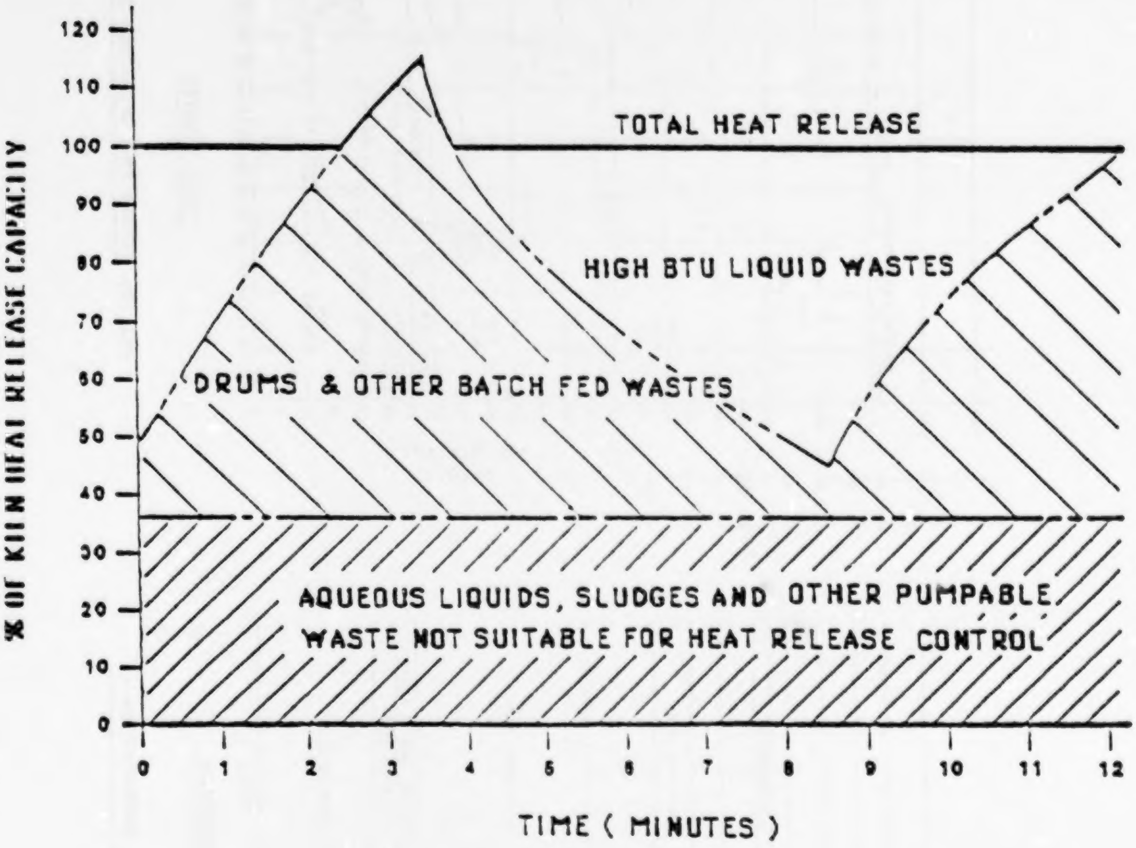
Solids Loading - 90 lb. (0.55 MM BTU) every 5 min.

CASE A   Volatilizes in 5 minutes
Equivalent Heat release : 16.77 MM BTU/HR

CASE B   Volatilizes in 3 minutes
Equivilant heat release : 21.12 MM BTU/HR

FIG. 9.

TYPICAL KILN HEAT RELEASE



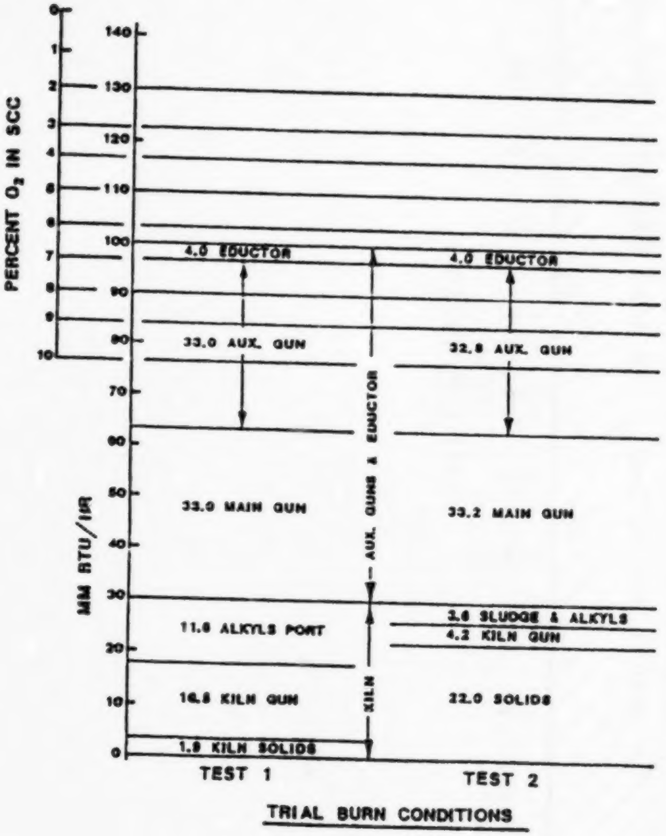


FIG. 10a. ROTARY KILN OPERATING DATA

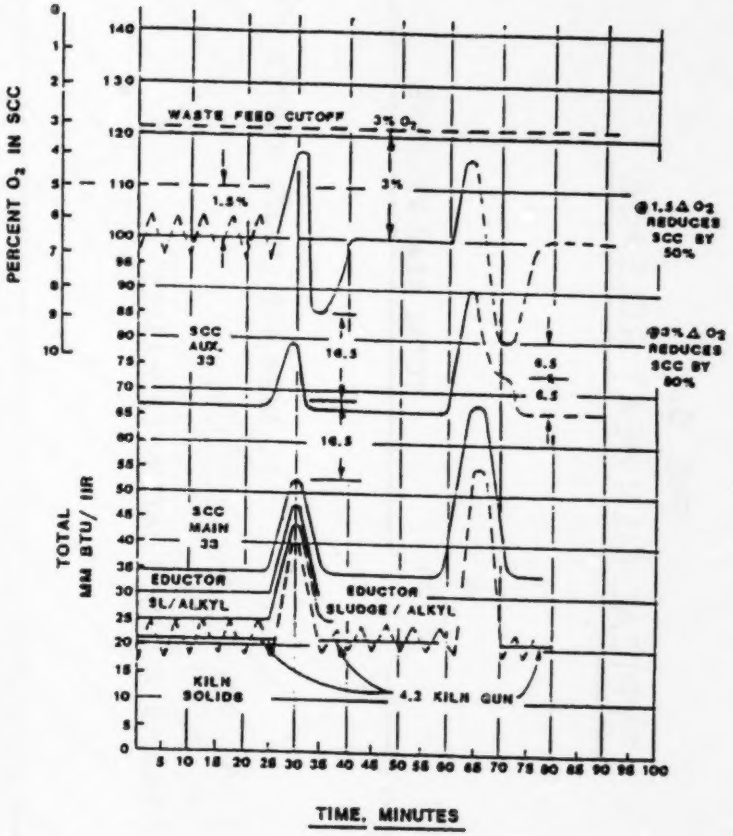


FIG. 10b. ROTARY KILN OPERATING DATA

THE USE OF OXYGEN IN HAZARDOUS WASTE INCINERATION -- A STATE-OF-THE-ART REVIEW

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Tarrytown, New York 10591

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ABSTRACT

The use of advanced oxygen combustion technologies in hazardous waste incineration has emerged in the last two years as one of the most significant breakthroughs among all the competing treatment technologies. Unlike most others, oxygen combustion technologies can be easily retrofitted onto various existing incinerators. The capacity of existing incinerators can typically be increased by a factor of two or three, and destruction and removal efficiencies (DRE's) can potentially be improved with such a retrofit.

For many years, industrial furnaces have used oxygen enrichment of the combustion air and oxygen-fuel burners, but with conventional technologies a high oxygen level generally poses problems. The flame temperature is high, leading to high NOx formation and local overheating. Different technical approaches to overcome these problems and their respective effectiveness will be reviewed. Previously, commercial oxygen enrichment in incinerators was limited to a rather modest level (less than 26% O2). This paper will review some of the recent commercial applications of much higher oxygen enrichment levels in hazardous waste incinerators.

The general characteristics of any oxygen enriched flame, the benefits that can be anticipated, and the associated economic ramifications are explored in this paper. Also reported are the results of recent EPA evaluations of two unique oxygen combustion technologies: The Pyretron™ burner by American Combustion, Inc. and the LINDE® Oxygen Combustion System by the Linde Division of Union Carbide Industrial Gases, Inc.

INTRODUCTION

In response to the Federal Resource Conservation and Recovery Act (RCRA) amendments of 1984 and Superfund Reauthorization and Amendments (SARA) of 1986, incineration is generally considered to be the most permanent solution of hazardous chemical waste treatment. RCRA includes a statement of national policy which emphasizes that "reliance on land disposal of hazardous waste should be minimized or eliminated...land disposal should be used as a last resort and should be replaced in most cases by advanced treatment, recycling, incineration and other hazardous waste control technologies." Incineration is a proven technology for treating a wide range of materials including liquid, solid, and semi-solid wastes such as PCBs, solvents, organic residues, halogenated hydrocarbons, pesticides, herbicides, and laboratory waste.(1,2) In addition, the continued discovery of abandoned hazardous waste sites as a result of Superfund investigations has placed increasing pressure on the U.S. Environmental Protection Agency (EPA) to find alternate solutions for treating and disposing of toxic and hazardous wastes. The decreasing availability of landfill sites and the increasing public opposition to toxic and hazardous waste transport have added to the pressure.

EPA's regulations for incineration of hazardous wastes require that the system must achieve a Destruction and Removal Efficiency (DRE) of at least 99.99 percent of the Principal Organic Hazardous Constituents (POHCs) present in the waste and at least 99.9999 percent for dioxin and PCB contaminated wastes. High excess air levels are generally used to ensure that the incinerators meet these high performance standards.

The use of oxygen or oxygen-enriched air in place of air for incineration can improve the overall performance and efficiency of chemical waste incinerators, and reduce the overall cost of the system. As oxygen replaces part or all of the air for incineration, the nitrogen portion is reduced in both the oxidant and the flue gas. Hence, the volume of the oxidant and the flue gas are reduced per unit of waste processed. In addition, the concentration of oxygen in the fuel-oxidant mixture is increased.

EFFECTS OF OXYGEN ENRICHMENT ON GENERAL COMBUSTION CHARACTERISTICS

Oxygen enrichment (21-100%) of air reduces the amount of nitrogen present as a diluent in the reaction of fuel and oxygen. The rate of combustion reaction usually increases significantly with oxygen enrichment due to the higher partial pressures of both oxygen and fuel and the resulting higher equilibrium temperature. This higher reaction rate is one of the main reasons for the following changes in the combustion characteristics(3):

- higher flame speed
- lower ignition temperature
- wider flammability range
- higher blow-off velocity gradients
- higher adiabatic flame temperature

For incineration applications it is necessary to evaluate how these changes affect flame stability, flame temperatures and safety of the process.

Flame Stability

In general, a higher flame speed will improve flame stability and create a more intense and shorter flame. It is, however, difficult to quantitatively predict the actual effects on industrial burner flames which are post mixed and turbulent.

The lower flammability limit (lean limit) of a fuel and air mixture is little influenced by oxygen enrichment of the air. This is expected since excess oxygen in the lean limit is considered to act as a heat sink similar to nitrogen(4). The higher flammability limit (rich limit), on the other hand, is extended substantially with oxygen enrichment, as shown in Table 1. For example, the higher flammability limit of methane is increased from 14% to 61% by going from air to pure oxygen. For all the fuels cited, the ratio of the limits expands greatly.

For burner applications, wider flammability limits generally correlate with greater flame stability. The change in the upper limit allows the combustion of the fuel or waste to begin even in a highly fuel-rich mixture.

Stability of a premixed flame can be measured in terms of the critical velocity gradients at blow-off limits. "Blow-off" is the condition of a burner flame where the flow velocities of the gases forming the combustible mixture exceed the burning velocity everywhere in the flow field. In such conditions, the combustion wave is driven back from the burner and loses its stable "anchor" in relation to the burner face. As much as 100-1000 fold increases in blowoff velocity gradients were measured when pure oxygen was used instead of air (7). The dramatic increases in the blow-off velocity gradients with oxygen enrichment are considered to improve flame stability for wide turn down ranges of firing rate. A higher blow-off limit is also advantageous in designing high velocity burners with good flame stability.

Adiabatic Flame Temperature

The adiabatic flame temperatures increase significantly with oxygen enrichment due to the reduction of nitrogen which acts as a diluent in combustion. The flame temperature increases by as much as 100°F for a 1% increase in oxygen concentration for low enrichment levels. The rate of increase in the flame temperature decreases gradually with the enrichment level and tapers off at high enrichment levels.

There are two main reasons for this phenomenon: (1) the amount of nitrogen eliminated with each unit percent oxygen enrichment diminishes with increasing enrichment level, and (2) endothermic dissociation of CO_2 and H_2O becomes increasingly significant at high temperatures. Table 2 lists adiabatic flame temperatures of selected fuels with air and oxygen at stoichiometric ratios.

Adiabatic flame temperature is the maximum flame temperature attainable under an ideal condition. The actual temperature of an industrial burner flame is significantly lower than the adiabatic flame temperature due to radiative heat loss and turbulent mixing with surrounding colder furnace gases.

It is important to recognize that the adiabatic flame temperature simply provides an upper limit in the attainable flame temperature and that higher flame temperature is not essential in increasing heat transfer in a furnace with oxygen enrichment. Special burners and oxygen enrichment techniques have been developed and applied in industries to increase heat transfer in a furnace without creating higher flame temperatures that might cause a local overheating problem(13-15). Further discussion on furnace heat transfer and flame temperature is given later in this paper.

Oxygen Safety

An important safety consideration resulting from higher reactivities and lower ignition temperatures in an oxygen enriched atmosphere is the material compatibility for oxygen service. Many materials which do not ignite in air can ignite in oxygen enriched atmospheres. Extensive studies have been conducted to evaluate metals, sealing materials and lubricants for oxygen service (8), and practical guidelines have been reported for piping (9,10), compressors, and pumps (11).

From the viewpoint of combustion safety, the potential to create a flammable mixture in a furnace prior to startup would increase if both the fuel and oxygen enriched air leak simultaneously. Thus, the prevention of accidental accumulation of oxygen enriched air in the furnace becomes an important design consideration for an oxygen-enriched combustion system.

ADVANTAGES OF USING OXYGEN

The main advantages of using oxygen for incineration can be summarized: (1) the fuel consumption, if supplemental fuel is required, is lowered primarily due to the reduced sensible heat loss to the flue gases; (2) the throughput of the incinerator, which is normally limited by the air blower capacity, the gas residence time and the size of the flue gas cleaning system when using air, can be significantly increased; (3) the DRE can potentially be improved due to the higher oxygen concentration in the fuel-oxidant mixture and longer residence time; (4) pollution control of the reduced flue gas is less costly and more effective; and (5) control of "puffs", as indicated by CO excursions, is achievable.

Fuel Savings with Oxygen

For the incineration of low BTU wastes such as aqueous waste and contaminated soil, very significant amounts of auxiliary fuel are consumed. In such a case, flue loss is usually the biggest single source of heat loss for a high temperature incinerator. In a typical waste incinerator fired with natural gas and cold air, about 50-70% of the higher heating value of the fuel is lost as sensible heat in the flue gas.

By replacing combustion air with oxygen, the corresponding reduction of nitrogen in the flue gas lowers the sensible heat loss dramatically. In Figure 1 the fuel required to provide 1 MM BTU of available heat to a furnace is plotted as a function of flue gas temperature for ambient air, enriched air, and oxygen. The "available heat" can be defined as the gross quantity of heat released within a combustion chamber minus the combustion flue gas loss. For this example, the fuel is methane and the oxygen concentration in the flue gas is 6 percent by volume. As the flue gas temperature increases, the fuel requirement to provide a given amount of energy above that temperature level increases, and the difference between air and oxygen as oxidants becomes greater. For example, as the temperature level increases from 1800°F to 2400°F, the fuel requirement to obtain 1 MM BTU of available energy increases from 2.2 to 6.1 MM BTU for air, and from 1.2 to 1.4 for oxygen. As a result, the fuel savings using oxygen increases substantially as the operating temperature of the furnace increases. Shown in Fig. 2 are the specific fuel savings by using oxygen enrichment in terms of MM BTU fuel savings per ton of oxygen, as a function of flue gas temperature and excess oxygen level.

Note that when the concentration of excess oxygen in the flue gas is increased for both the air and oxygen combustion systems to the same level, fuel efficiency of the air system deteriorates much faster than that for the oxygen system. Consequently, fuel savings by switching from air to oxygen becomes greater when the concentration of excess oxygen in the flue gas is higher. In addition, when the system throughput is increased with oxygen enrichment, further fuel savings can be realized.

Throughput Increases

Oxygen enrichment has been successfully used for throughput increases in a broad range of industrial furnaces(3,16-19). Production increases of 10-20% are typically possible with a few percent increase in oxygen concentration for most furnaces.

The extent of throughput improvements possible for a particular incinerator depends on the nature of the incinerator limitations. Some of the typical limitations are listed in Table 3. The most common limitations are those related to the capacity limitations of fuel and air supply systems and the flue handling system including the air pollution control devices. Oxygen enrichment is very effective in overcoming these limitations due to the reduction of the volume of oxidant and flue gas for the same fuel input and higher available heat to the furnace. Such benefits are especially significant for a low BTU waste which requires auxiliary fuel input. Shown in Figure 3, as an example, is the relative flue gas volume as a function of oxygen enrichment to obtain the same available heat.

In the incineration of medium BTU waste (2000-8000 BTU/lb) with oxygen enrichment, by reducing and in some cases eliminating the use of auxiliary fuel, the thermal capacity of an incinerator can be dedicated to the combustion of hazardous waste instead of auxiliary fuel. Throughput increase in this manner can often be achieved. Even for incineration of high BTU waste where auxiliary fuel is not required, a specific flue gas volume reduction can be achieved with oxygen enrichment in conjunction with the use of waste water injection.

The dust carryover problem, a common process limitation, is related to particle size, characteristics of the particulate matter, and the aerodynamic patterns within the kiln. Although the improvement by using oxygen can not be accurately predicted, the lower kiln superficial gas velocity should be beneficial in reducing the dust carryover. For example, dust carryover problems in cement, lime and hazardous waste rotary kilns have been effectively alleviated by the lower flue gas volumes resulting from oxygen enrichment(17,19,20).

In many cases the capacity of an incinerator is limited by the mechanical design of the system. Mechanical modifications must be made in order to overcome such limitations before oxygen enrichment can be useful.

For the incineration of low-BTU wastes, such as contaminated soil, the heat transfer rate to the heat load may be a rate-limiting factor. High temperature oxygen/oxygen-enriched flames have been successfully applied to certain glass melters and kilns to increase heat transfer to strategic areas in the vessels. In most waste incinerators such as a rotary kiln, however, a high temperature flame can cause overheating of the refractory walls and possible slagging problems. On the other hand, an extremely high temperature flame is not essential to achieve a higher overall heat transfer rate. Gas radiation from hot combustion products to the surrounding refractory walls and re-radiation to the heat load is the primary mode of heat transfer in most high temperature furnaces. The intensity of gas radiation is not only a function of gas temperature and concentrations of CO_2, H_2O, and soot, but also is strongly influenced by the volume of the radiating gas. The volume of a flame is usually a small fraction of the entire furnace. Thus, in a radiation dominant furnace with temperature limitations, the preferred condition for productivity improvement is to increase the average gas temperature of the heat transfer zone by enhancing the temperature uniformity, rather than by a localized increase in flame temperature. The above principle should be applied intelligently to maximize the benefit of oxygen-enriched combustion.

Performance Improvements

It is sometimes argued that the high flame temperature achievable with oxygen enrichment is conducive to higher DREs due to improved oxidation kinetics. However, studies have shown that with a temperature above 2000°F, the combustion reaction is limited by the rate of mass transfer processes of oxygen and toxic molecules (i.e. atomization, evaporation and mixing), rather than the kinetic rates, the contribution of extremely high temperatures being quite limited. Therefore, a flame with high momentum and moderate temperature may be most suitable for incinerator applications. EPA studies have also shown that well-run conventional air-based incineration systems achieved very high DREs at temperatures between 1800°F to 2200°F(1,21).

On the other hand, EPA studies and pilot scale tests also show that the performance of incinerators could deteriorate significantly during some upset conditions (or so called "failure modes")(22,23). Oxygen enrichment can alleviate many of the failure modes. One of the important failure modes is the occurrence of flameout. This failure mode can clearly benefit from oxygen enrichment which improves flame stability. Poor atomization, low combustion temperature and slow evaporation of liquid waste have been cited as important failure modes (24). Although atomization of waste depends mostly on the burner system design, oxygen enrichment has been shown to improve evaporation of liquid waste by raising the intensity of the flame and therefore improving the burnout efficiency of waste (25).

Transient Emissions Control

Another important failure mode is transient emissions (puffs) from incinerators. When high-BTU wastes are fed into rotary kiln incinerators in an intermittent mode, the transient combustion behaviors of these materials create unsteady releases of combustible gases which may momentarily exceed the oxygen supply to the incinerator. These temporary oxygen-deficient conditions can cause the release of products of incomplete combustion (PICs) which are often called "puffs". These "puff" phenomena have raised public concerns recently and have been the subject of research projects sponsored by the EPA (26,27).

It has been suggested that the higher partial pressure of oxygen in the combustion chambers available with oxygen enrichment, can alleviate the temporary oxygen-deficient conditions. This approach, the subject of a recent EPA study reporting mixed results, is discussed later in this paper (28). In addition, it should also be noted that too high an oxygen level is not only inefficient, but may also cause high NOx emission level (28). Therefore, oxygen enrichment, per se, may not be an ideal solution to the transient puff problem.

On the other hand, advanced process control techniques utilizing advanced process sensors and dynamic oxygen injection can reduce puff occurrences significantly (20). Properly designed computer-control algorithms can automatically adjust the amount of oxygen according to unforeseen changes in the heating value of the waste.

Such benefits are more difficult to achieve with conventional air systems. The main reason for this difficulty is that the critical process variables of temperature, residence time and oxygen feed are inter-dependent when combustion air is used. For example, an increase in the excess oxygen level in the combustion chamber would carry enough associated nitrogen to lower the temperature and the residence time of combustion gases and possibly cause the loss of kiln vacuum.

If oxygen is used in place of air for excess oxygen level control, and auxiliary fuel and/or dynamic water spray is used to control incinerator temperature variations, the above process variables can be controlled independently without adversely affecting the others.

TECHNICAL CONSIDERATIONS IN THE USE OF OXYGEN IN INCINERATION

For many years industrial furnaces have used oxygen enrichment of the combustion air and oxygen-fuel burners, but with conventional technologies a high enrichment level may pose problems. The flame temperature is typically high, leading to potentially high NOx formation and local overheating.

Various techniques exist for introducing oxygen into industrial furnaces. The selected technique depends on the desired results and the present limitations of the furnace. Oxygen enrichment can be achieved quite inexpensively through routine enrichment of the combustion air. However, general enrichment techniques are typically limited to a level of 5 percent (26 percent oxygen in the oxidant) due to increased flame temperatures.

Oxygen-enriched combustion can also be accomplished by strategically injecting the oxygen into the furnace using either lances or oxy-fuel burners. Undershot lancing of the existing air-fuel burners is a beneficial technique for significant production increase in most rotary kilns. The advantage of this method over general enrichment is that only the segment of the flame facing the solid bed (load) is enriched. The bulk of the main flame shields the refractories from the high flame temperature produced at the point of oxygen impingement.

Oxygen-fuel burners, which offer greater flexibility in heat distribution, are applicable for production increases as high as 100%. Conventional oxygen-fuel burners also tend to produce a high temperature flame and high NOx formation. They are used quite commonly in applications such as auxiliary burners in electrical arc furnaces for scrap melting, and recently in glass melting furnaces.

In order to overcome the disadvantages associated with conventional oxygen combustion technologies noted above, the patented LINDE® Aspirator Burner (or "A" Burner) was developed by the Linde Division of Union Carbide (31,32). The key feature of the "A" Burner is that the furnace gases are aspirated into the oxidant jets prior to mixing with the fuel, as explained in references 32 and 33. By maintaining sufficient distance between high velocity oxygen jets and the fuel flow, enough of the furnace gases can be aspirated into the oxygen jet prior to mixing with the fuel so that the resulting flame temperature can be reduced to a value equivalent to an air flame temperature. Gas mixing and recirculation within the furnace are accomplished by the mixing effect of the high velocity oxygen jets, which results in a uniform temperature distribution within the incinerator.

Nitrogen Oxides

The nitrogen oxides (NOx) emissions due to thermal fixation of ambient nitrogen are strongly dependent on the flame temperature. They depend not only on the particular burner design, but also on the furnace temperature, the post-flame oxygen partial pressure, and the nitrogen content of the furnace gases. A recent study sponsored by the Department of Energy (DOE)(35) obtained extensive NOx data on various oxygen-enriched combustion conditions. The burners tested represented both conventional air-fired designs and oxygen/fuel burners designed primarily for very high oxygen levels. The four burners tested were:

- Bloom® Engineering Hot Air Burner
- Maxon Kinemax® Burner
- Maxon/Corning Oxytherm® Burner
- LINDE "A" Burner

The Bloom Burner and the Maxon Kinemax Burner are conventional air-fired designs. These two burners were selected for this project as representative of a large number of current industrial furnace installations. These burners are not necessarily optimized for oxygen-enriched air firing or low emissions. They are typical examples of industrial burners with non-water cooled refractory burner tiles. The Oxytherm Burner was developed jointly by Maxon and Corning Glass for the application of oxygen/fuel combustion in glass furnaces. The burner is also a non-water cooled refractory design with a specially designed refractory exit which shapes the flame while withstanding high flame temperatures. The Oxytherm Burner tested was designed for operation with essentially pure oxygen, that is, 90-100 percent oxygen, as the oxidant. The design basis for the LINDE "A" Burner was discussed earlier.

Referring to Figure 4, this DOE study showed that for conventional air burners NOx emissions increased sharply (up to 2.2 lb NOx/MMBTU) as the level of oxygen enrichment was increased in the range of 35-50 percent oxygen. However, the LINDE "A" burner showed low NOx emissions for the entire range of 35-100 percent oxygen. The lowest NOx emissions were achieved at 100 percent oxygen (0.01 to 0.03 lb/MM BTU) due to the low partial pressure of nitrogen in the furnace. However, for incinerators under even a slight vacuum, close to 100% oxygen would be very difficult to achieve due to the inevitable air infiltration.

More recently, in the EPA Mobile Incinerator trial burn tests using the LINDE "A" Burner (20), NOx emissions were 0.07 to 0.18 lb/MMBTU. In a separate pilot test using the Pyretron(TM) Burner by American Combustion, Inc., EPA reported NOx levels that averaged between approximately 1.1 to 2.6 lb/MMBTU. More details are given in a later section on these results.

Flame Temperature and Furnace Temperature Distributions

In the DOE study, the different burners demonstrated distinct axial radiant heat flux distributions which changed by varying degrees as the level of oxygen enrichment was increased. Linde's "A" Burner demonstrated the ability to vary its flame patterns and thus heat flux distributions by employing interchangeable oxygen nozzles.

Due to the varying characteristics of waste feeds in hazardous waste incinerators, the control of temperature distribution is both challenging and important. Local hot spots can cause potential refractory damage, and more frequent clinker formation or slag buildup (slagging), which requires eventual shutdown of the furnaces for slag removal. These slags are masses of ash material which have deformed and fused together. This is a condition which occurs approximately between 1800°F and 2500°F; however, the presence of low melting point ash and metals in the waste feed may cause the formation of eutectic solutions with substantially lower melting temperatures. Suspended solid particles can also be melted in a hot flame and later redeposited onto the refractory wall.

The geometric configuration of an incinerator, e.g. a long and narrow rotary kiln, may also present a special challenge in heat distribution. Therefore, the ability of an oxygen-enriched burner system to control both its flame temperature and the furnace temperature distribution in a hazardous waste incinerator is critical in order to achieve the maximum benefits.

RECENT TECHNICAL AND COMMERCIAL DEVELOPMENT

While oxygen combustion is used more commonly in the metal industries, its use for full-scale hazardous waste incineration is now emerging.

ENSCO/Pyrotech tested the use of oxygen enrichment up to 50% O_2 in an early liquid injection mobile incinerator for the destruction of PCBs (36). This system used a water-cooled burner block to withstand the high flame temperature (over 4000°F). Extremely high NOx emissions (over 5000 ppm) and burner maintenance problems were cited as deterrents to the use of oxygen. In addition, ENSCO's original incentive for using oxygen was to achieve a high flame temperature, but they found that such temperatures were not necessary to achieve a 99.9999% destruction and removal efficiency (DRE) (37).

According to a recent review paper (6), ThermalKEM (formerly Stablex) in

Rock Hill, South Carolina, has been using oxygen enrichment on their (35 MM BTU/hr) Consumat dual chamber incinerator since 1986 by enriching the combustion air to the upper chamber (afterburner) to the 25-26% O_2 level. Reportedly, this technique was successful in eliminating high CO excursions caused by batch loading of solid wastes.

In Japan, a bench-scale oxygen burner was developed by Nippon Sanso K.K. to incinerate pure PCBs at about 5 lb/hr. Excellent destruction efficiency was reported (>99.9999%) with a temperature more than 2700°F (38).

In Europe, during 1985(39) Union Carbide Europe (UCE) in conjunction with Studiecentrum voor Kernenergie (SCK) in Mol, Belgium successfully replaced an air-oil burner with an oxygen-oil burner in a small high temperature slagging incinerator treating radioactive and hazardous waste, doubling the capacity. A scale-up unit of a similar design will be operational in 1989.

In addition, UCE has been assisting a customer in France since July 1987 in using oxygen enrichment at a large commercial rotary kiln incinerator. Originally the slow evaporation of water from the liquid wastes led to a long and lazy flame which extended the length of the combustion chamber. Oxygen enrichment of up to 24% is used to shorten the flame length significantly. It also helps to stabilize the burner operation despite product inconsistencies and variations. A 100% production increase of liquid waste with low to medium heat content (900 to 5000 Btu/lb) was effected from the use of oxygen enrichment (25).

Recently, the U.S. EPA has evaluated separately two modern oxygen combustion technologies using dissimilar approaches: the LINDE Oxygen Combustion System by the Linde Division of Union Carbide Industrial Gases Inc. and the Pyretron burner(30) by American Combustion Inc. (ACI). The Pyretron burner was tested earlier in a bench scale rotary kiln simulator at the EPA Research Triangle Park (RTP) Laboratory. It was later tested in a pilot scale rotary kiln incinerator at the EPA Combustion Research Facility (CRF) in Arkansas. Test results for both programs have been recently reported. The pertinent conclusions about oxygen combustion with the ACI burner from the RTP test were(28):

(1) It is hard to draw conclusions regarding the individual effects of oxygen enrichment on transient puffs due to the confounding effects of temperature, oxygen partial pressure, and total oxygen feed rates.

(2) Oxygen enrichment may cause unacceptable emissions of NOx. Concentrations as high as 1500 ppm (corrected at 7 percent oxygen) were reported for higher oxygen enrichment levels (up to 30%).

In the CRF test of the ACI burner conducted in late 1987(29), the waste stream selected for the test was a mixture of waste material from the Stringfellow Superfund site and decanter tank tar sludge (listed waste K087). The resulting waste stream had a heat content of approximately 8600 BTU/lb. The base test using air burners had a feed rate of 105 lb/hr. The maximum feed rate using Pyretron burners in both the kiln and the afterburner was 210 lb/hr. Water injection was used to control temperature in the kiln. In all tests DREs exceeded 99.99%. The effect of the Pyretron on transient emissions could not be directly ascertained. Transient emissions, as measured by CO spikes, were obtained during operation of both the air burner and the Pyretron burner. However, the pattern of these emissions showed too much variability to conclusively state whether the Pyretron reduced transient emissions. NOx data have recently been reported for these tests (45). NOx emission levels from this operation of the American Combustion burner system averaged 725 ppm to 1753 ppm at about 9% CO_2 and 15% O_2 (approximately 1.1 to 2.6 lb NOx/MMBTU).

A LINDE Oxygen Combustion System was installed in the EPA Mobile Incineration System (MIS) in June, 1987 to replace an air burner on the rotary kiln (20,40). The LINDE pure oxygen burner normally supplied over 60% of the overall oxygen in the kiln, the rest coming principally from the kiln air leakage. The capacity of the modified MIS was more than doubled with the use of oxygen. The original maximum throughput of dioxin contaminated soil was about 2000 lb/hr. The system capacity was easily increased to 4000 lb/hr as confirmed by certified verification tests. Based on these test results, a RCRA Part B permit was extended and modified for the EPA MIS. Also, trial burn tests of the unit with PCBs and other RCRA listed POHCs in solid and liquid matrixes showed DREs surpassing EPA standards at solid waste feed rates of about 4000 lb/hr.

According to the trial burn results(41), NOx emission levels from the Linde oxygen system averaged between 54.6 and 138.3 ppm at about 15% CO_2 and 7% O_2 (0.07 to 0.18 lb NOx/MMBTU) which compare favorably with the data from the previous air system levels obtained in the 1985 trial burn(42) (between 126-166 ppm at about 11% CO_2 and 7% O_2 or 0.19 to 0.235 lb NOx/MMBTU). Also for the incineration of solid wastes with high heat content, kiln "puffs," as measured by CO spikes, were virtually eliminated with the help of Linde's proprietary oxygen feedforward-feedback system. It was found that the tendency of the rotary kiln to slag was not aggravated from the use of the LINDE Oxygen Combustion System when the flame pattern was adjusted correctly. This experience has shown that when the system is operated with a good understanding of the process and waste feed characteristics, the occurrence of slagging is minimal (43).

The EPA MIS, after its modifications, was used to decontaminate more than 5 million pounds of soil from several dioxin-contaminated sites in southwest Missouri. EPA has found that it is both more economical and more reliable to use the modified Mobile Incinerator equipped with the LINDE Oxygen Combustion System than the previous air system (43). Since the EPA Mobile Incinerator is to date the only incinerator in the U.S. with a RCRA permit to incinerate dioxin contaminated waste, EPA used the modified MIS to incinerate over 2 million pounds of brominated sludges contaminated with dioxin from sites in southwestern Missouri(43,44).

Recently, the LINDE Oxygen Combustion System has also been demonstrated successfully in a transportable incinerator with a system capacity many times greater than the EPA MIS. Results of this installation will be published at a later date. Also, the Army Corps of Engineers recently awarded a $52 million incineration contract for a major Superfund site to a contractor using the LINDE Technology.

ECONOMICS

With all the technical benefits, the success of oxygen combustion technologies also depends on the economic impact of using oxygen. The principal economic benefit from oxygen combustion is derived from the very significant throughput improvement. The large fixed portion of daily incinerator operating costs (typically $10,000 to $30,000 per day) is spread over a much larger quantity of waste processed. For example, for mobile/transportable incinerators a doubled throughput can reduce the allocated incineration cost of contaminated soil by typically $100 to $500 per ton of waste, while the cost of oxygen required is typically less than $50 per ton of waste incinerated.

In addition, whenever supplemental fuel is required for incineration, the fuel savings by using oxygen can offset the cost of oxygen and often show a net cost savings based on fuel savings alone. The economics of using oxygen to save fuel, of course, depend on the relative cost of fuel and oxygen. For example, at the EPA MIS a remarkable specific fuel savings of 50 million Btu per ton of oxygen used was demonstrated (20). Assuming a No. 2 fuel oil cost of $0.60 per gallon or $4.40 per million BTU, the break-even oxygen cost is $220 per ton of oxygen. The actual cost of oxygen ranges from about $50 per ton of oxygen produced by a large on-site facility to about $120 per ton for delivered liquid oxygen.

CONCLUSION

Recent technology innovations have demonstrated the significant advantages of using oxygen in the field of hazardous waste incineration. Common concerns associated with conventional oxygen combustion such as local overheating and high NOx emission are valid. Advancements in combustion technology to overcome those problems have been demonstrated in extended field operations.

While the general principles discussed in this paper would apply to most situations, the best method to employ oxygen varies with each individual incineration system as well as with the profiles of the waste feed. The application of sophisticated technological know-how is often required. The process economics also change from site to site and need to be analyzed on a case by case basis, although frequently the benefits of oxygen far exceed its cost if used intelligently. The increasing use of oxygen combustion in commercial incineration applications speaks well for its economic and technical attractiveness.

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Table 1

COMPARISON OF FUEL FLAMMABILITY LIMITS IN AIR AND OXYGEN (5,6)

Fuel	Flammability Limits (vol% fuel)			
	Lower		Higher	
	Air	O_2	Air	O_2
Hydrogen, H_2	4	4	74	94
Carbon monoxide, CO	12	16	75	94
Ammonia, NH3	15	15	28	79
Methane, CH4	5	5	4	61
Methylene Chloride	*	16	*	66
Vinyl chloride	4	4	22	70

* Not flammable in air

Table 2

APPROXIMATE FLAME TEMPERATURES OF SELECTED FUELS AT STOICHIOMETRIC RATIOS (12)

Fuel	Air		Oxygen	
	K	°F	K	°F
Acetylene	2600	4220	3410	5680
Carbon monoxide	2400	3860	3220	5340
Heptane	2290	3660	3100	5120
Hydrogen	2400	3860	3080	5080
Methane	2210	3520	3030	4990

Table 3

EFFECTIVENESS OF OXYGEN ENRICHMENT FOR THROUGHPUT INCREASE

Limitations	Effectiveness of O_2/O_2-Enrichment
THERMAL CAPACITY	Effective
Air Blower	
Fuel Supply	
Burner	
Incinerator Draft	
Air Pollution Control System	
Combustion Gas Residence Time	
DUST CARRYOVER	Effective
MECHANICAL SOLID PROCESSING CAPACITY	No Effect
HEAT TRANSFER	Conditionally Effective

Figure 1

FUEL REQUIREMENT TO PROVIDE 1 MM BTU OF AVAILABLE HEAT

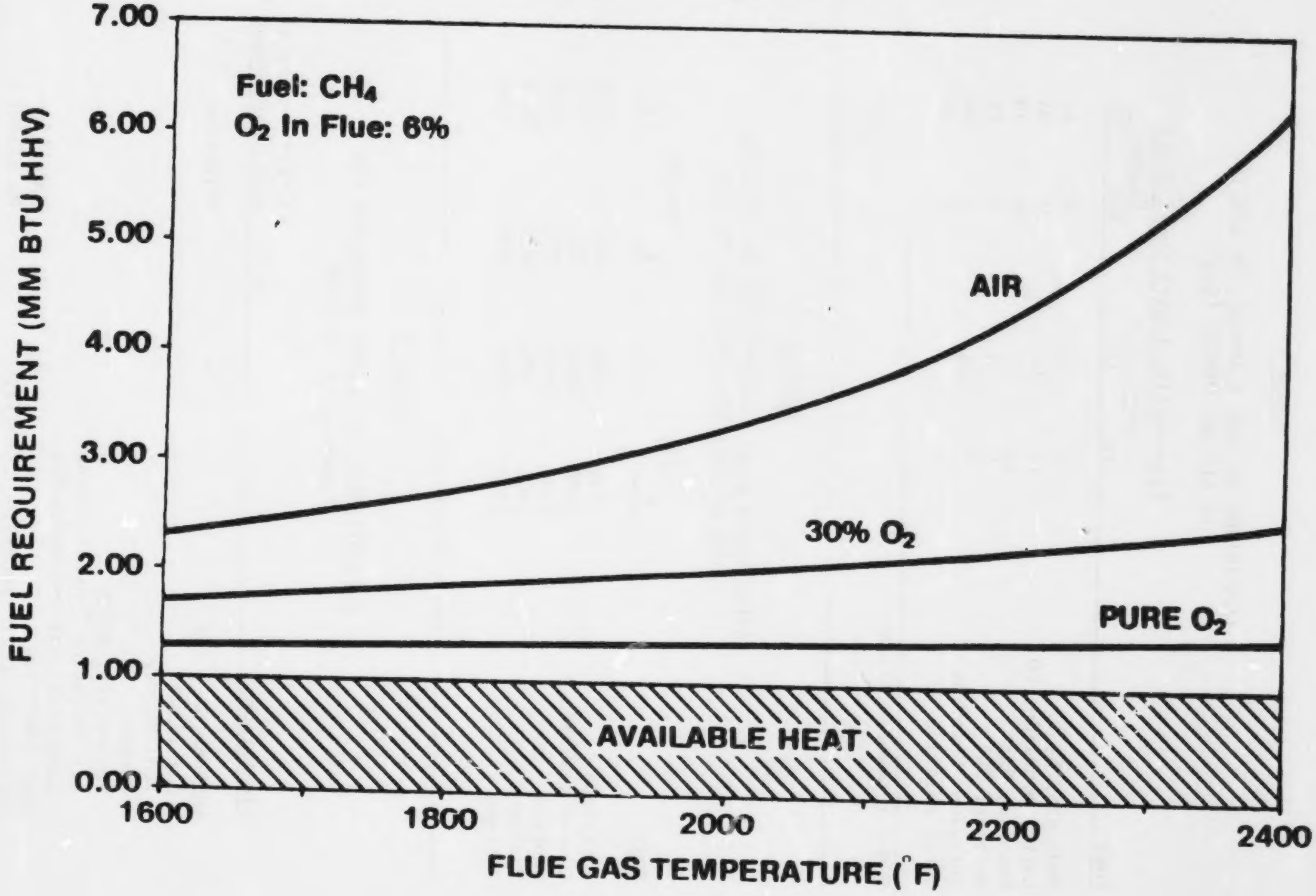


Figure 2

FUEL SAVING WITH OXYGEN - METHANE GAS

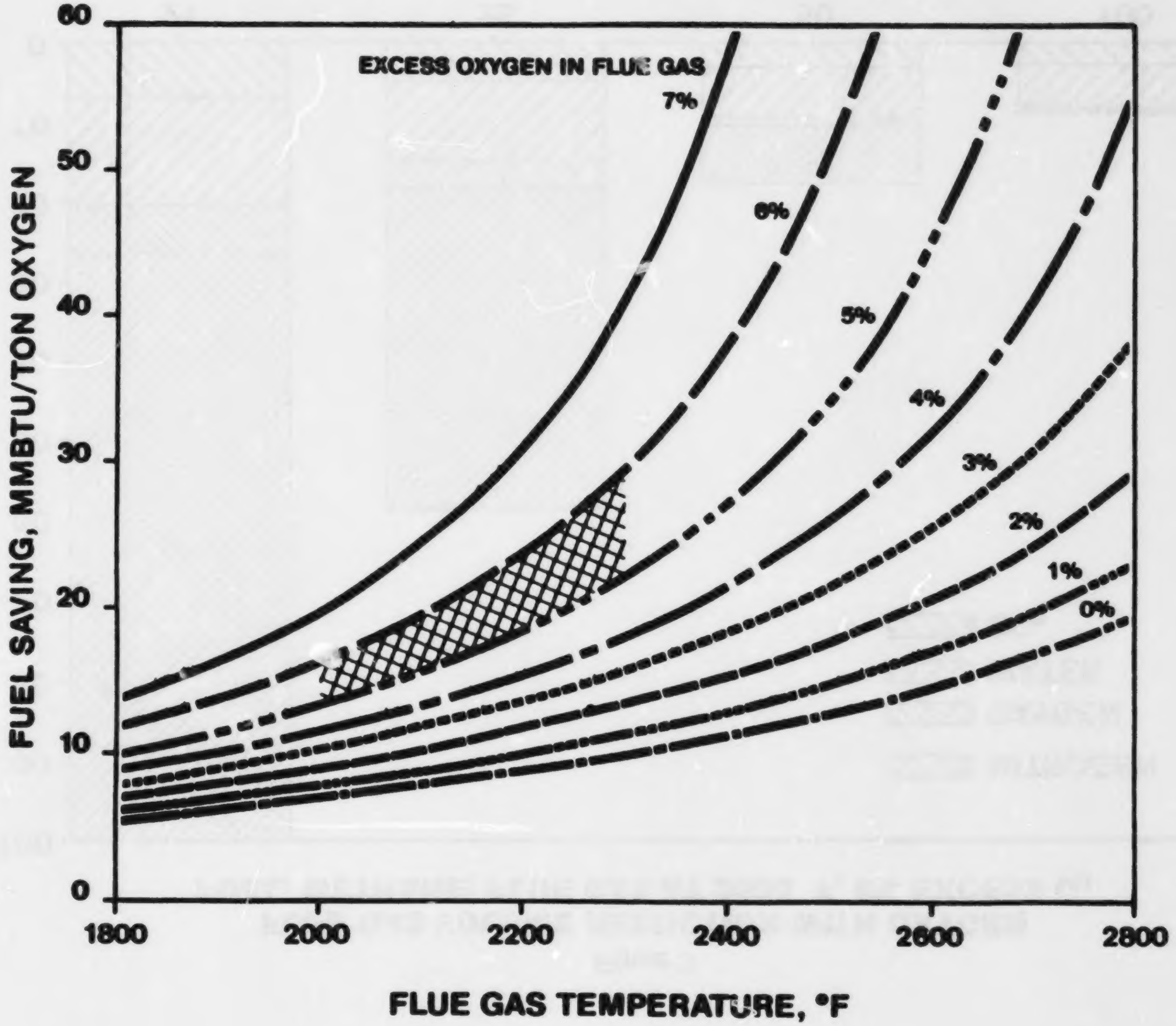


Figure 3

FLUE GAS VOLUME REDUCTION WITH OXYGEN
FUEL: METHANE; FLUE GAS AT 2000 °F, 6% EXCESS O_2

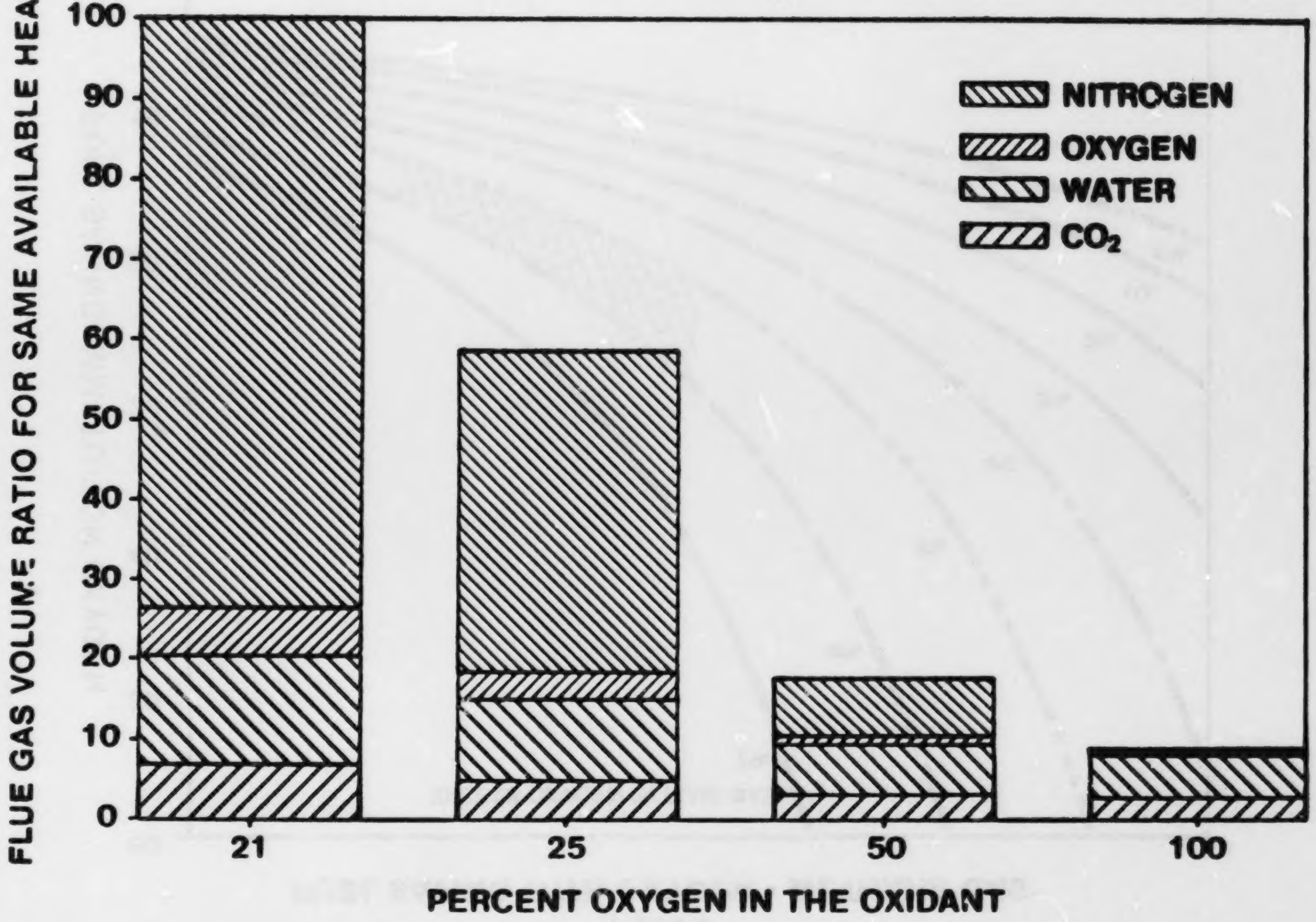
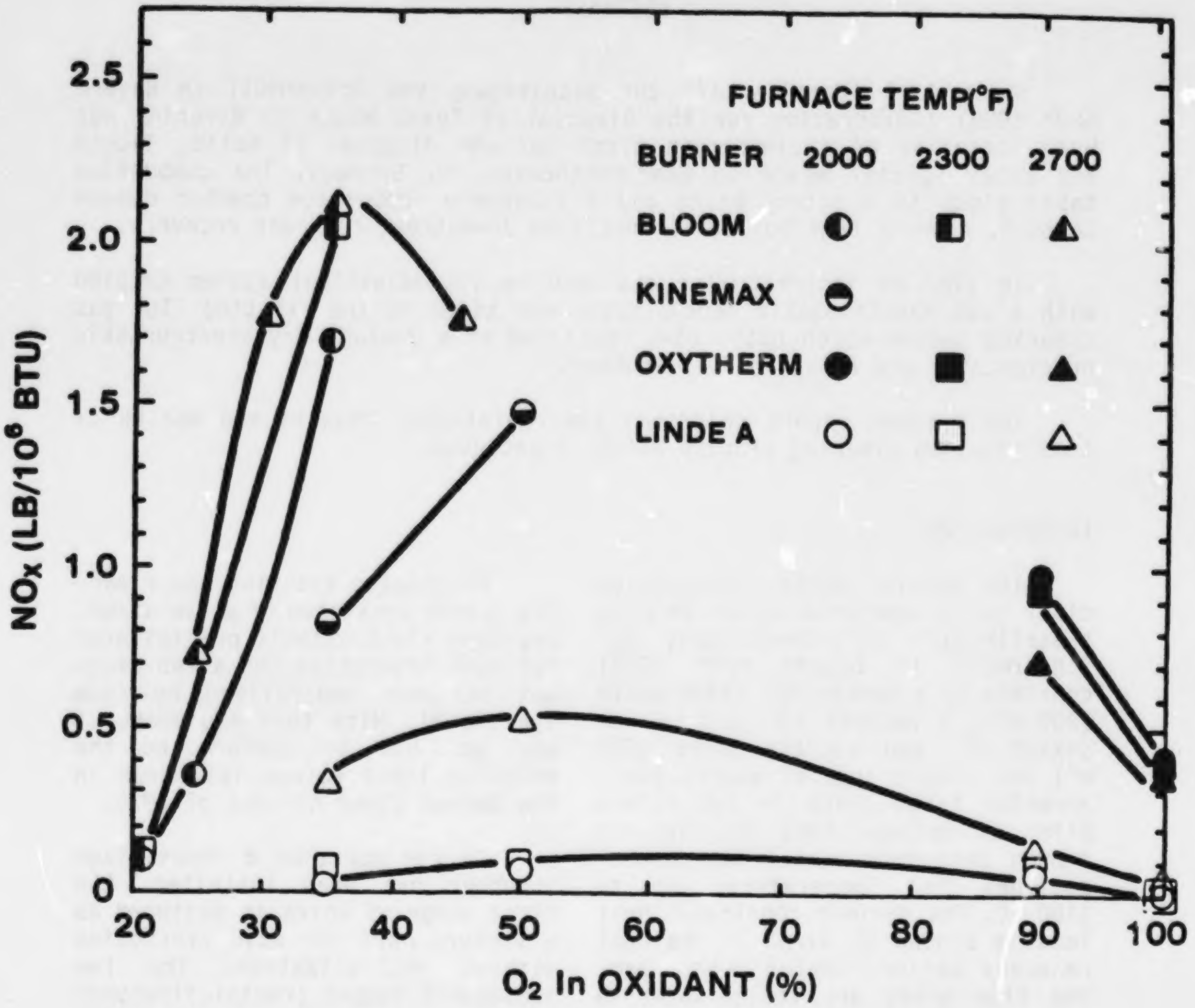


Figure 4

SUMMARY OF NO_X EMISSIONS

FUEL: NATURAL GAS EXCESS O_2 = 2% (DRY)

SOURCE: DOE STUDY



FLUE GAS CLEANING BY WET SCRUBBING AND CONDENSATION IN A SPECIAL WASTE INCINERATION PLANT

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ABSTRACT

Since 1976 "Gesellschaft zur Beseitigung von Sondermüll in Bayern mbH" (GSB) (Corporation for the Disposal of Toxic Waste in Bavaria) has been operating an incineration plant for the disposal of solid, liquid and pasty special waste in Baar-Ebenhausen, W. Germany. The combustion takes place in 2 rotary kilns and 1 secondary combustion chamber common to both. A waste heat boiler is installed downstream for heat recovery.

In 1987 an indirect flue gas cooling (condensation) system coupled with a wet electrostatic precipitator was added to the existing flue gas cleaning system which until then consisted of a 2-stage dry electrostatic precipitator and a 3-stage wet srubber.

The present report describes the operational results and merits of this combined cleaning process which is patented.

INTRODUCTION

The special waste incineration plant being operated since 1976 by "Gesellschaft zur Beseitigung von Sondermüll in Bayern mbH" (GSB) consists of a bunker for solid waste (900 m³), 4 bunkers for pasty waste (4x100 m³) and storage tanks (650 m³) for liquid special waste. Incineration takes place in two rotary kilns at approx. 1000 °C, and one common secondary combustion chamber designed for temperatures up to 1400 °C. The maximum continuous heat load is around 52 GJ/h. In the heat recovery boiler located downstream, the flue gases are cooled down to approx. 280 °C, thereby producing abt. 30 t/h of steam (270 °C, 28 bar) which is used for the generation of nearly 2 MW of electric power.

Originally the flue gas cleaning system consisted of a two-stage, dry-type electrostatic precipitator for dust separation and a two-stage wet scrubber neutralized by soda lye (NaOH). With this equipment it was possible to conform to the emission limit values laid down in the German Clean Air Act of 1975.

In the meantime a three-stage scrubber has been installed, the first stage of which is designed as a venturi part for acid processing without neutralization. The two subsequent stages (radial-flowtype) operate on neutral processing with soda lye. Limestone ($CaCO_3$) and lime milk $Ca(OH)_2$ are used for external neutralization of the discharge from the acid scrubber stage.

PURPOSE

The Ebenhausen incinerator being sited close to a military base, the maximum waste gas stack height had to be limited to 28 m. Without corrective measures, which were taken in the event, this would have meant polluting the adjacent area with inadmissibly high emissions. On top of that the German Clean Air Act of 1986 laid down even more stringent emission values which - after a grace period - had to be complied with by existing plants, too. As a result, GSB was forced to retrofit additional flue gas cleaning facilities for its incinerator in line with the statutory requirements.

APPROACH

The aim of retrofitting was to minimize the amount of fine dust particles as carrier of heavy metals and toxic organic compounds passing through the existing flue gas cleaning system including mist eliminator after the wet scrubber. (Original limit value for dust emission: 50 mg/m³, present: 30 mg/m³, referred to standard conditions, dry, 11 % O_2). In particular the mercury emission rate had to be reduced considerably.

After an extensive study of the technical possibilities and after performing a series of tests [1-2], the following process was selected for further reducing the residual pollutants:

- Cooling down the steam-saturated flue gases after the scrubber with the formation of mist as a result of the microscopic dust particles in the gas providing nucleii for the condensation of steam.
- Passing of this mist into a wet electrostatic precipitator and separation.
- Reheating with hot air and removal of the dry flue gases.

This process combination is protected by letters patent [3].

Following tests in which a partial gas stream was cooled down from 65 °C to 20 °C after the scrubber and considerable amounts of heavy metals including mercury were found in the condensate, a pilot plant was installed at the Ebenhausen facility. By means of a tubular cooler the influence of temperature reduction through direct and indirect flue gas cooling was examined and the efficiency of condensation compared with that of the wet-type electrostatic precipitator. These investigations revealed that formation of the mist by condensation was of vital importance to the final cleaning of the flue gas.

Finally, cooling down by about 15 °C proved to be the best compromise between operational economy and collection efficiency of mercury, utilizing the latter as a reference parameter for the determination of plant efficiency as also other heavy metals and the noxious HCl and HF gases. Under these conditions the condensate produced could be absorbed by the scrubber water circuit.

In the test the collection rates for mercury ranged between 55 % and 80 %, for the heavy metals cadmium, chromium, copper, iron, nickel, lead and zinc, as well as for arsenic between 90 % and >99 %, and for hydrofluoric acid between 94 % and 96 %. Thus the collection efficiency to be expected for the overall cleaning system, comprising dry electrostatic precipitator, scrubber and condensation with wet-type electrostatic precipitator, was 80 - 92 % for mercury and more than 99.9 % for the other parameters.

In contrast to the collection efficiencies of the other heavy metals - which were consistently high irrespective of the initial concentration - precipitation of mercury was subject to wide fluctuations. On the whole, initial concentrations of mercury of upto 0.6 mg/m³ were reduced to values below 0.2 mg/m³ in the clean gas to comply with the requirements of the 1986 Clean Air Act.

PROBLEMS ENCOUNTERED

Retrofitting of the indirect flue gas cooling (condensation) system and wet electrostatic precipitator to the existing flue gas cleaning system at the Ebenhausen incinerator had to be performed taking due account of the following requirements:

- Integration into the existing flue gas cleaning system without impairing its proven service reliability, in the place available, and within a period of 3 weeks (scheduled downtime for maintenance), with the possibility of restoring the original state (bypass) for retrofitting.
- No production of additional solid waste or effluents.
- Replacement of the I.D. fan by a system designed for new pressure conditions.
- Reasonable operating costs.
- High service reliability.

RESULTS

Process Description

The flue gas cleaning system retrofitted by Lurgi at the end of 1987 at investment costs of 7.2 million DM is shown schematically in Fig. 1.

About 77,000 m³/h (standard, wet) flue gas at appr. 280 °C flow from the two-stage dry electrostatic precipitator into the venturi inlet of the three-stage wet scrubber. 87,000 m³/h (standard, wet) flue gas at 65 °C leave the scrubber and are cooled by 15 °C in two carbon tubular coolers operated in parallel. Here 10 m³/h condensate are produced, while 77,000 m³/h (standard, wet) of flue gases at 50 °C are led into the downstream wet electrostatic precipitator, where the mist drops formed by cooling are separated (appr. 0.5 m³/h). The flue gas is heated up with hot air to 75 °C and exhausted into the atmosphere via an induced draft fan and a stack.

The coolers are operated with 700 m³/h of circulating water which is recooled in a tubular forced-air heat exchanger. Given the location of the incinerator, river water as cooling medium was ruled out as was the use of an evaporative cooler.

The condensate from cooling and the electrostatic precipitator together with 1.5 m³/h spray water for wetting the electrodes in the wet electrostatic precipitator is taken to the lower scrubber water circuit. During flue gas cooling 10 m³/h evaporate from the upper, first scrubber water circuit. Furthermore 6 m³/h are withdrawn from this acid water circuit for external neutralization and heavy metal precipitation. The total water balance is kept constant by adding

4 m³/h fresh water to the lower water circuit.

The energy consumption of the retrofitted third flue gas cleaning stage is 200 kW on an average, and the pressure drop is 22 mbar.

Emissions

Messrs. Ecoplan performed the acceptance tests of the retrofitted flue gas cleaning system in May, 1988. The measuring points shown in Fig. 1 are marked A-D. 4 series of measurements were taken under the following operating conditions:

- Measurement series 1: normal pollutant-load in raw gas feeding at app. 120 % flue gas volume
- Measurement series 2: normal feeding at 100 % flue gas volume
- Measurement series 3: increase of noxious substance at appr. 120 % flue gas volume
- Measurement series 4: increase of noxious substance at appr. 100 % flue gas volume.

Each series consisted of six half-hour measurements. The results taken from the measuring report of Ecoplan are compiled in table 1. The results will be published in detail elsewhere [4].

In summary it can be stated that the flue gas leaving the dry electrostatic precipitator is still dust-laden. The acid noxious gases correspond to the load of the pollutants in the raw gas. On account of the temperature, mercury at measuring point A is in the gas phase.

In the three-stage wet scrubber, besides HCl and HF (not measured), a part of dust, and, to a certain extent, SO_2 are separated. Whereas in the acid scrubber stage the mercury content is reduced considerably, a proportion of aerosols, volatile mercury compounds and metallic mercury are still left behind [5]. The condensation stage is the governing factor in the further elimination of mercury. The microscopic dust particles are also removed with the condensate.

Finally the wet electrostatic precipitator proves to be an efficient fine cleaning system:
In all the emissions dust is no longer traceable. Thus heavy metals are no longer present in the solid phase. HCl and HF are far below the limit values (50 mg/m³ and 2 mg/m³ respectively). Total mercury is separated with an efficiency of 86 % to 98 %, and the remainder is in elementary form. The other heavy metal contents measured are in the gas phase as well.

Further emission measurements were performed by TÜV Bayern (Technical Inspectorate of Bavaria) in June 1988 with a series of 6 to 8 half-hour measurements. Table 2 shows the average values obtained.

The SO_2 measurements are partly unsatisfactory and thus point to the system limits. For this particular parameter the guarantee values (<100 mg/Nm³ at a raw gas load up to 1000 mg/Nm³) have not been achieved. Summed up for all measurements, the efficiency of SO_2 separation ranges between 48 % and 70 %, and thus is not satisfactory at high raw gas concentrations. In the meantime it has been proved [6,7] that SO_2 can also be separated in the acid pH phase, and that the oxygen dissolved in the scrubber water is the limiting factor for SO_2 oxidation to sulfate in the acid range as well. Therefore, SO_2 emissions can be minimized by an optimum control of excess oxygen, the temperature, the pH value and the mass transfer areas (large surface due to mist formation through condensation).

In the meantime Gesellschaft für Arbeitsplatz- und Umweltanalytik GbR haS proved in addition that organic emissions, too, can be minimized with the effectively flue gas cleaning combination described above. The mean collection rates achieved were as follows:

Penta- und hexachlorobenzenes	23 %
Sum of penta- to decachlorinated biphenyls	33 %
Sum of tetra- to octachlorinated dibenzofurans	67 %
Sum of 11 polycyclic aromatic hydrocarbons	83 %
Sum of tetra- to octachlorinated dibenzo(p)dioxins	93 %
Sum of 9 polycyclic aromatic hydrocarbons (without the more volatile fluoranthene and pyrene)	99.5 %

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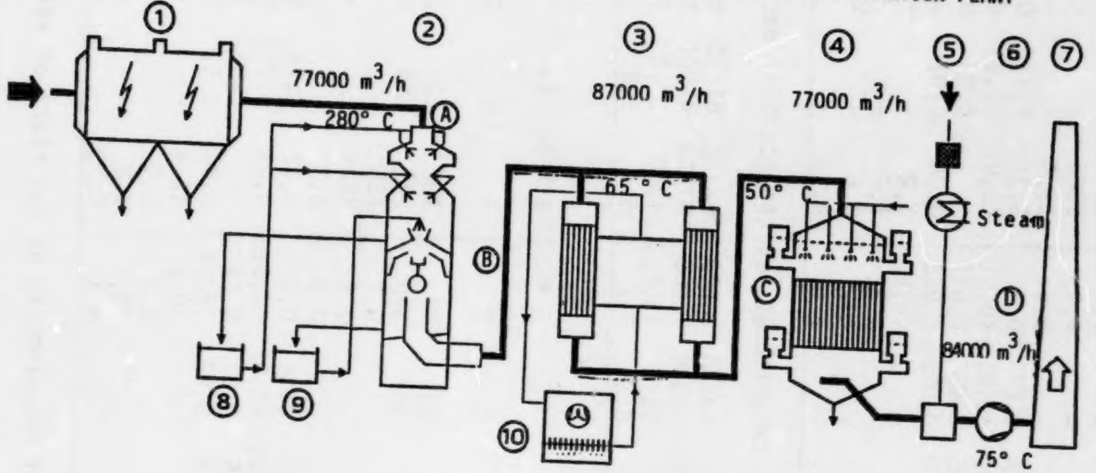
The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Figure 1

Rauchgasreinigung FLUE GAS CLEANING
Sondermüllverbrennungsanlage SPECIAL WASTE INCINERATION PLANT


①
②
③
④
⑤
⑥
⑦
77000 m³/h
280° C
Ⓐ
87000 m³/h
65 ° C
Ⓑ
77000 m³/h
50° C
Ⓒ
Steam
Ⓓ
84000 m³/h
75° C
⑧
⑨
⑩

1. Dry Electrostatic Precipitator
2. Wet Scrubber
3. Flue Gas Cooling System
4. Wet Electrostatic Precipitator
5. Flue Gas Reheating System
6. I.D. Fan
7. Stack
8. Acid Stage
9. Basic Stage
10. Water Recooling System

(I.D. = induced draft)

Water Balance	
10 m³/h evaporation	12 m³/h condensation lower water circuit
6 m³/h phys.-chem. treatment	4 m³/h make-up water (fresh water)

Table 1 Average values of 6 half-hour measurements each

Emission [mg/m^{3}n dry]	1st series				2nd series			
	A	B	C	D	A	B	C	D
Dust	68,2	57	31,2	<3	94,5	53	28	<3
SO_2	114	85	41	38,2	292	128	112	97
HF	344	-	-	0,8	69	-	-	0,3
HCl	5317	-	-	4,0	3002	-	-	9,6
C total	6,3	-	-	3,6	11,4	-	-	5,4
Hg total	0,068	0,096	0,07	0,04	0,31	0,11	0,07	0,02
Hg particles	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Hg (0)		0,035	0,03	0,035		0,04	0,02	0,02
Hg volatile	0,07	0,062	0,028	0,012	0,30	0,07	0,04	<0,01
Zn particles	3,53	-	-	<0,1	1,2	-	-	<0,1
Zn volatile	1,63	-	-	1,32	1,0	-	-	2,1
Pb particles	1,12	-	-	<0,1	0,6	-	-	<0,1
Pb volatile	0,18	-	-	1,12	0,13	-	-	0,58
	Random measurements at the start of each series							
V wet [m^{3}n/h]	76200	74900	64900	83500	68100	61790	62720	66800
V dry	56500	57800	56500	75200	57800	47900	54680	60900
O_2 [%]	11,1	11,3	11,2	13,1	10,8	12,8	12,2	13,4
CO_2 [%]	6,3	6,3	6,3	5,2	6,4	5,8	6,0	5,0

Emission [mg/m^{3}n dry]	3rd series				4th series			
	A	B	C	D	A	B	C	D
Dust	131	81	54	<3	202	63	33	<3
SO_2	705	561	407	310	845	293	298	238
HF	520	-	-	0,7	165	-	-	0,4
HCl	4974	-	-	2,5	4984	-	-	2,4
C total	8,4	-	-	3,8	8,3	-	-	8,0
Hg total	1,83	0,59	0,34	0,04	0,88	0,15	0,05	0,03
Hg particles	<0,01	<0,01	<0,01	<0,01	0,01	0,015	0,01	0,01
Hg (0)		0,06	0,02	0,04		0,063	0,045	0,023
Hg vol.	1,82	0,52	0,20	<0,01	0,87	0,07	0,07	<0,01
Zn particles	7,6	-	-	<0,1	15,4	-	-	<0,1
Zn volatile	0,7	-	-	1,3	1,0	-	-	1,2
Pb particles	3,7	-	-	<0,1	5,9	-	-	<0,1
Pb volatile	<0,1	-	-	0,4	0,13	-	-	0,33
	Random measurements at the start of each series							
V wet [m^{3}n/h]	74300	82500	67400	87300	70400	89600	68700	7100
V dry	64000	63500	57600	76100	60400	52500	52800	65300
O_2 [%]	10,6	11,2	11,2	15	12,9	11	11,3	15,4
CO_2 [%]	6,5	6,3	6,2	4,1	5,5	6,4	6,1	3,9

Table 2 Emission mean values of dust constituents [mg/m^3 n], dry, 11 % O_2

		Limiting value
Hg total	0,123	Σ = 0,2
Cd	0,00003	
Tl	< 0,00009	
As	< 0,00045	Σ = 1
Cr (IV)	0,00036	
Co	< 0,00009	
Ni	< 0,00009	
Se	< 0,00045	
Te	< 0,00009	
Pb	0,00171	Σ = 5
Cu	0,00027	
Mn	0,00018	
V	< 0,00009	
Sn	< 0,00045	
Sb	0,00126	
Cr (VI)	< 0,00036	
CN^-	< 0,00045	
F^-	0,00478	

EVALUATION OF MECHANISMS OF PIC FORMATION IN LABORATORY EXPERIMENTS: IMPLICATIONS FOR PIC FORMATION AND CONTROL STRATEGIES IN FULL-SCALE INCINERATION SYSTEMS

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ABSTRACT

It is generally agreed that products of incomplete combustion (PICs) are produced from hazardous waste incinerators burning chlorinated hydrocarbons (CHCs), although to what degree they are formed and their effect on human health and the environment remain controversial issues. Laboratory studies indicate that the high-temperature thermal decomposition behavior of CHCs is highly complex and generally involves the formation of many intermediate species before thermodynamic equilibrium is achieved. In this manuscript, a quantitative description of these processes for the simplest of CHCs, the chlorinated methanes, is presented. Specific emphasis is given to PIC formation reaction channels for chloroform and carbon tetrachloride, which are often observed in full-scale systems. Potential PIC formation and control strategies for these compounds and their decomposition products are presented based on the rate-limiting reaction channels observed.

INTRODUCTION

Control of emissions of toxic organic compounds from incinerators burning hazardous materials is one of the major technical and sociological issues surrounding the further implementation of thermal destruction as a waste disposal alternative [1]. Laboratory, pilot, and full-scale studies have produced data indicating that properly designed and operated facilities can achieve the destruction of toxic organic waste feed components to environmentally acceptable levels [2-5]. However, total organic emissions from the incinerator effluent are seldom fully characterized. This has led to both scientific and public concern over possible emissions of toxic products of incomplete combustion (PICs) from the incineration of toxic materials under less than ideal conditions [6,7].

Dellinger et al. [8,9] have presented data that strongly suggests that the relative destructive efficiencies (DEs) of principal organic hazardous constituents (POHCs) are controlled by high-temperature, thermal decomposition kinetics in the post-flame regions of incinerators. Dellinger et al. [8,9] and Tsang [10] have suggested that poor mixing of waste and oxygen in these regions is responsible for emissions of undestroyed POHCs [6-10]. This result may be extrapolated to PIC formation processes, as theory and experiment indicate that oxygen-starved conditions are responsible for most PIC emissions since the rate of POHC destruction is significantly slowed and the rate of PIC formation is substantially increased [11,12].

As a first step towards developing guidelines for predicting full-scale PIC emissions, PIC formation and destruction mechanisms for simple chlorinated hydrocarbons (CHCs) are being evaluated using precisely controlled oxygen-starved laboratory flow reactor experiments [13]. Results indicate that the high-temperature thermal decomposition behavior of CHCs is highly complex and generally involves the formation of many intermediate species. A series of elementary reactions, which often constitute a radical chain mechanism, are believed to control the nature and concentration of intermediates in this kinetically limited system. Dellinger et al. [12-14] have previously discussed in a qualitative manner general mechanisms of waste destruction and PIC formation for simple CHCs, e.g., chlorinated alkanes, and more complex CHCs, e.g., chlorinated benzenes, PCBs, etc. In this manuscript, a more quantitative description of these processes is presented for the simplest of CHCs, the chlorinated methanes. Specific emphasis is focused on PIC formation pathways for chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4), which are often observed as emissions from full-scale tests [4,5]. Potential PIC formation and control strategies for these compounds and their decomposition products are also presented based on the rate-limiting reaction channels observed.

EXPERIMENTAL DESCRIPTION

The laboratory results presented in this manuscript were generated using the Thermal Decomposition Analytical System (TDAS) [15,16]. The thermal decomposition unit of the TDAS consists of a high-temperature fused silica tubular reactor in which a flowing gas stream, exhibiting a segregated flow pattern, is exposed to temperatures as high as 1100°C for mean residence times of 0.5 to 6.0 s. Reactor design ensures that samples experience a square-wave thermal pulse with a very narrow, near-Gaussian, residence time distribution. Heated, fused silica transfer lines (250°C) connect the insertion chamber to the reactor and the reactor to the effluent analysis system. The analytical function of the TDAS is conducted by a HP 5890B programmed temperature gas chromatograph and a 5970A Mass Selective Detector. Data reduction is achieved with a HP 59970 ChemStation and the accompanying system software which includes an on-line NIH-EPA mass spectral library.

RESULTS

The high-temperature, gas-phase, thermal decomposition behavior of chloromethane (CH_3Cl), methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4) were evaluated under the following conditions: residence time = 2.0 s, fuel/oxygen equivalence ratio = 3.0 (oxygen-starved), reactor concentration = 2×10^{-5} moles/liter, temperature range = 300-1000°C [14]. The decomposition profiles of CH_3Cl, CH_2Cl_2, and $CHCl_3$ were accurately modeled using the reaction pathways and kinetic rate parameters shown in Table 1. The composition of the radical pool which governs bimolecular destruction pathways was estimated using a pseudo-equilibrium calculational approach [17].

Three-center concerted HCl elimination is the principal decomposition pathway for $CHCl_3$, accounting for greater than 99% of the decay at the 99% DE level (600°C). HCl elimination and

Table 1

Chlorinated Methane Decomposition Rate Parameters[a]

Cmpd	ΔH°_{300} (kcal/mole)[b]			$\log k_{300}$		
	C-Cl	HCl Elim.	H abst. (Cl)	C-Cl[c] (1/s)	HCl Elim.[d] (1/s)	H abst. (Cl)[23] (cm^3/mol-s)
CH_3Cl	82.8	83.6	-3.0	15.40-82.5/2.3RT [22]	14.0-90.0/2.3RT	13.5-3.3/2.3RT
CH_2Cl_2	80.0	67.3	-4.0	16.42-79.7/2.3RT	14.1-69.0/2.3RT	13.4-3.0/2.3RT
$CHCl_3$	77.6	49.6	-7.8	16.19-77.4/2.3RT	14.3-54.5/2.3RT [25]	12.8-3.3/2.3RT
CCl_4	70.3	-	-	16.30-70.0/2.3RT	-	-

Footnotes:

a Pathways from left to right are unimolecular C-Cl bond fission, unimolecular 3-center HCl elimination, and bimolecular H abstraction by Cl.

b Thermodynamic data obtained from reference 18.

c Except where noted, Arrhenius pre-exponential coefficients were calculated by transition state theory. Arrhenius activation energies were calculated by subtracting 0.5RT [24] from the reaction enthalpy.

d Except where noted, Arrhenius pre-exponential coefficients were calculated by transition state theory. Arrhenius activation energies were estimated from a limited database of 3-center HCl elimination reactions.

C-Cl bond rupture represent approximately 95% and 3% of the destruction of CH_2Cl_2 at the 99% DE level (780°C), respectively. Due to the relative strength of the C-Cl bond in CH_3Cl as compared to the other chloromethanes, unimolecular C-Cl bond rupture and concerted HCl elimination make relatively small contributions (42% and <1%, respectively) to the decomposition of this compound at the 99% DE level. As a result, H atom abstraction by Cl atoms make a significant contribution (57.5%) to the CH_3Cl decay at the 99% DE level (910°C).

The thermal decomposition profile for CCl_4 could not be accurately modeled by initiation processes involving C-Cl bond fission and Cl abstraction reactions. The experimental data suggested that a high-temperature POHC reformation pathway was operative for this molecule. As the following paragraphs demonstrate, construction of radical chain mechanisms which are consistent with thermochemical considerations can be used to identify which reaction pathways are responsible for PIC formation and POHC reformation at elevated temperatures.

Under identical experimental conditions, we have also evaluated the yields and stability of PICs produced from the thermal decomposition of the chloromethanes [14]. Results indicated that $CHCl_3$ and CCl_4 produced significant yields of chlorinated products (cf. Figures 1 and 2) while CH_3Cl and CH_2Cl_2 produced primarily low molecular weight hydrocarbons and HCl. Since the chlorinated products are of greatest interest due to their potential toxicity, we will now focus our attention on determining the rate-determining pathways which produce these products from the higher chlorinated methane precursors.

Inspection of Figure 1 indicates that the major initial organic reaction products from the $CHCl_3$ decomposition are tetrachloroethene (C_2Cl_4), CCl_4, and hexachloroethane (C_2Cl_6). The initial formation of C_2Cl_4 is consistent with a mechanism involving HCl elimination followed by recombination of dichlorocarbene biradicals (CCl_2). However, the formation of the remaining products indicates that a more complex set of reactions must also be kinetically significant. A preliminary elementary reaction kinetic mechanism (including reaction enthalpies and estimated kinetic rate parameters) which qualitatively accounts for the major products observed from $CHCl_3$ (and CCl_4) decomposition is given in Table 2. The initiation, chain branching, transfer and termination reactions were selected based on the observed products and thermochemical considerations as outlined by Benson [18].

As already mentioned, the main initiation reaction for $CHCl_3$ is concerted HCl elimination (R1). However, (R2) is also important as this chain branching reaction produces trichloromethyl radicals (CCl_3) and an exponential increase in the radical concentration. Two of the major products, C_2Cl_6 and CCl_4, are produced directly by reactions involving CCl_3 radicals, (R11) and (R3), respectively. A quasi-steady-state analysis indicated that Cl atom and C_2Cl_5 radical concentrations were small compared to the concentration of CCl_2 and CCl_3 radicals at temperatures less than 650°C [18]. The Cl concentration becomes slightly greater than the CCl_3 concentration (~50%) at higher temperatures. CCl_2 recombination (R10) and CCl3 recombination (R11) are the most significant termination reactions below 650°C while CCl_3 + Cl (R12) and Cl + Cl + M (R13) are most signifcant at higher temperatures.

Figure 3 presents a comparison of the rates for the potential pathways of C_2Cl_6 consumption (R6, R7, and R8). At low temperatures, Cl abstraction by CCl_3 radicals (R8) dominates. At higher temperatures, C-C bond fission (R6) and C-Cl bond fission (R7) become more kinetically significant. Further analysis indicates that C_2Cl_4 formation is dominated by recombination of CCl_2 radicals (R10) at low temperatures and (R8) followed by decomposition of the pentachloroethyl (C_2Cl_5) radical (R9) at higher temperatures (> 600°C). The C_2Cl_4 production rate decreases at temperatures greater than 650°C due to an increase in (R6) versus (R7) and (R8). This is in reasonable agreement with the experimental data in Figure 1. Additional comparison of the relative rates of CCl_4 formation indicates that, for temperatures less than 575°C, CCl_4 is produced by both Cl abstraction by CCl_3 radicals (R3,R8) and radical recombination (R12).

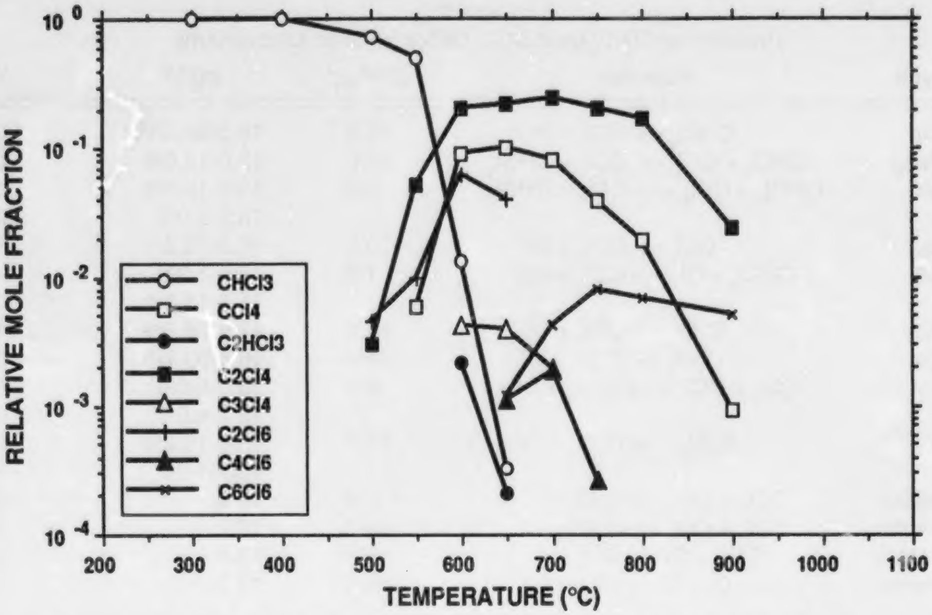

Figure 1. Thermal behavior of $CHCl_3$ and its associated products. See text for experimental conditions.

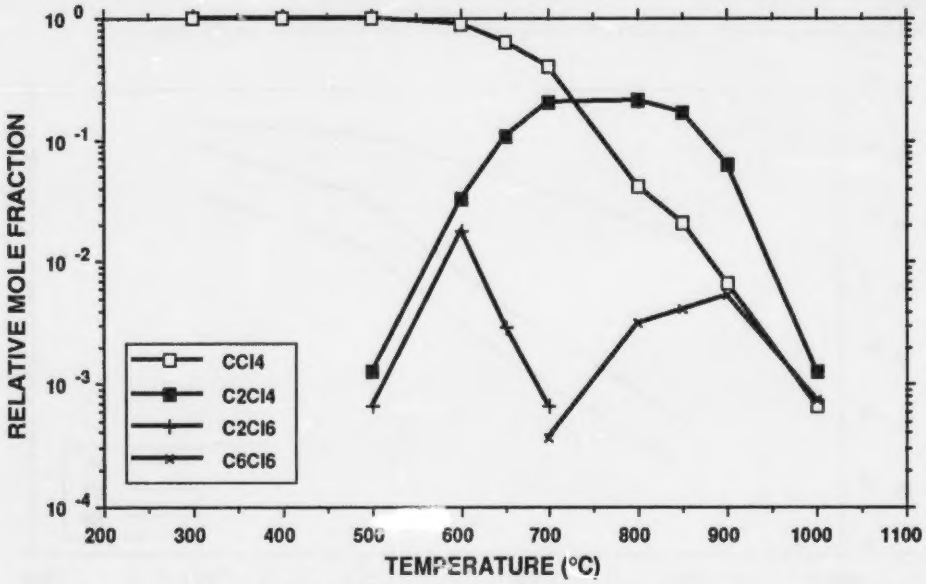

Figure 2. Thermal behavior of CCl_4 and its associated products. See text for experimental conditions.

Table 2
Preliminary $CHCl_3$ (and CCl_4) Decomposition Mechanisms

Rxn Type	Reaction	ΔH°_{300}[a]	log k[b]	Ref.
1. initiation	$CHCl_3 \rightarrow CCl_2 + HCl$	49.6	14.3-54.5/θ[c]	25
2. branching	$CHCl_3 + CCl_2 \rightarrow CCl_3 + CHCl_2$	10.8	13.0-14.0/θ	d
3. transfer	$CHCl_3 + CCl_3 \leftrightarrow CCl_4 + CHCl_2$	6.9	13.0-10.0/θ	d
			13.2-5.0/θ	d
4. initiation	$CCl_4 \rightarrow CCl_3 + Cl$	70.3	16.3-70.0/θ	13
5. transfer	$CHCl_3 + Cl \leftrightarrow CCl_3 + HCl$	-7.8	12.8-3.3/θ	23
			11.6-11.3/θ	23
6. initiation	$C_2Cl_6 \rightarrow CCl_3 + CCl_3$	69.1	17.5-68.8/θ	19
7. initiation	$C_2Cl_6 \rightarrow C_2Cl_5 + Cl$	70.0	16.8-69.7/θ	19
8. transfer	$C_2Cl_6 + CCl_3 \leftrightarrow C_2Cl_5 + CCl_4$	-0.3	13.0-5.0/θ	d
			12.7-5.0/θ	d
9. transfer	$C_2Cl_5 \leftrightarrow C_2Cl_4 + Cl$	17.2	15.8-16.2/θ	23
			12.2-1.0/θ	23
10. termination	$CCl_2 + CCl_2 \rightarrow C_2Cl_4$	-117.4	13.0	d
11. termination	$CCl_3 + CCl_3 \rightarrow C_2Cl_6$	-69.1	12.7	23
12. termination	$CCl_3 + Cl \rightarrow CCl_4$	-70.3	13.8	23
13. termination	$Cl + Cl + M \rightarrow Cl_2 + M$	-58.0	14.9	23

Footnotes:

[a] Reaction enthalpies calculated from data available in references 18 and 26.

[b] Units of reaction enthalpies and rate constants are cm^3, mole, s, kcal.

[c] θ = 2.303RT.

[d] Estimated from a large kinetic data base for similar reactions; see references 18, 23, and 27.

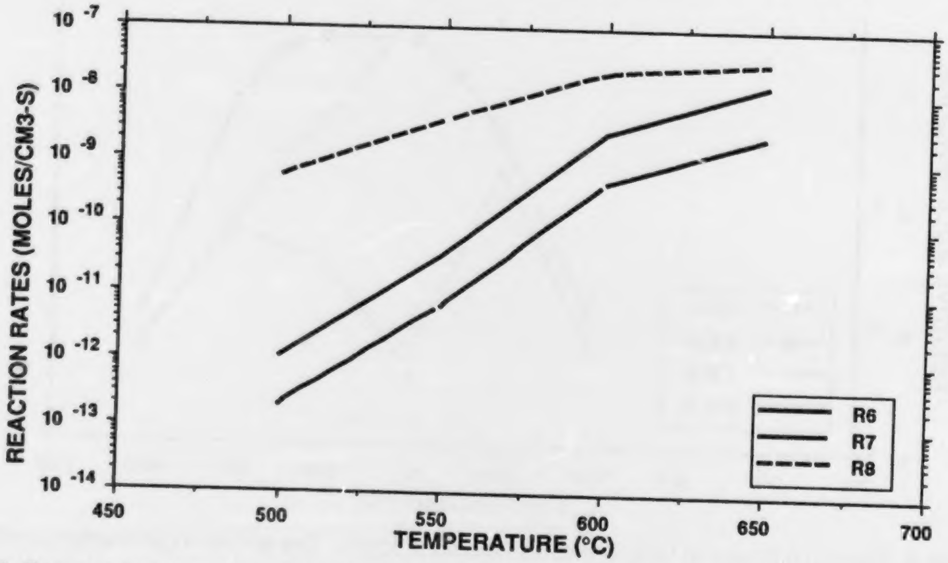

Figure 3. Comparision of reaction rates of C_2Cl_6 consumption from $CHCl_3$ thermal decomposition. See Table 2 for a description of the $CHCl_3$ decomposition mechanism and rate parameters.

At higher temperatures, (R12) dominates.

The mechanism of CCl_4 decomposition (see Table 2) producing C_2Cl_6 and C_2Cl_4 as the major products is largely a subset of the $CHCl_3$ mechanism. C-Cl bond rupture (R4) is the initiation step. A quasi-steady-state analysis for temperatures less than 800°C indicated that Cl atoms and CCl_3 radicals were in highest concentration with the Cl:CCl_3 ratio ~ 1.5. This ratio is expected to be maintained at higher temperatures.

Figure 4 presents a comparison of rates for three different pathways of C_2Cl_6 decomposition (R6, R7, and R8). The results are similar to those for $CHCl_3$. At low temperatures, Cl abstraction by CCl_3 radicals (R8) dominates. Analysis of the reaction rate of an analogous bimolecular reaction, Cl abstraction by Cl atoms, indicated that this reaction was kinetically insignifcant at all temperatures. At higher temperatures, unimolecular decomposition of C_2Cl_6 becomes faster than bimolecular attack. Analysis of the relative rates of C-C bond fission (R6) and C-Cl bond fission (R7) indicates that (R6) is nearly an order of magnitude faster at all temperatures. The C_2Cl_4 production rate thus decreases at temperatures greater than 650°C due to an increase in (R6) versus (R7) and (R8). This is in reasonable agreement with the experimental data in Figure 2.

A major difference between the $CHCl_3$ and CCl_4 mechanisms is the nature of the initiation and chain branching step. Formation of HCl followed by rapid reaction of CCl_2 with the parent compound reduces the probability of $CHCl_3$ reformation. For CCl_4, no chain branching step is possible. Furthermore, formation of CCl_4 (R8) and the reversibility of initiation (R12) compete with the consumption of CCl_4 by other routes. The importance of these reactions is evidenced by the slow decomposition of CCl_4 as illustrated in Figure 2.

DISCUSSION

In this manuscript, we have not considered destruction pathways for C_2Cl_4. In research being conducted concurrently, we are investigating reaction channels leading to the higher molecular weight products shown in Figures 1 and 2, i.e., hexachlorobutadiene (C_4Cl_6), and hexachlorobenzene (C_6Cl_6) [12,13,19]. These products have also been observed in molecular beam sampling of premixed trichloroethylene/oxygen/argon flat flames [20]. We feel that the

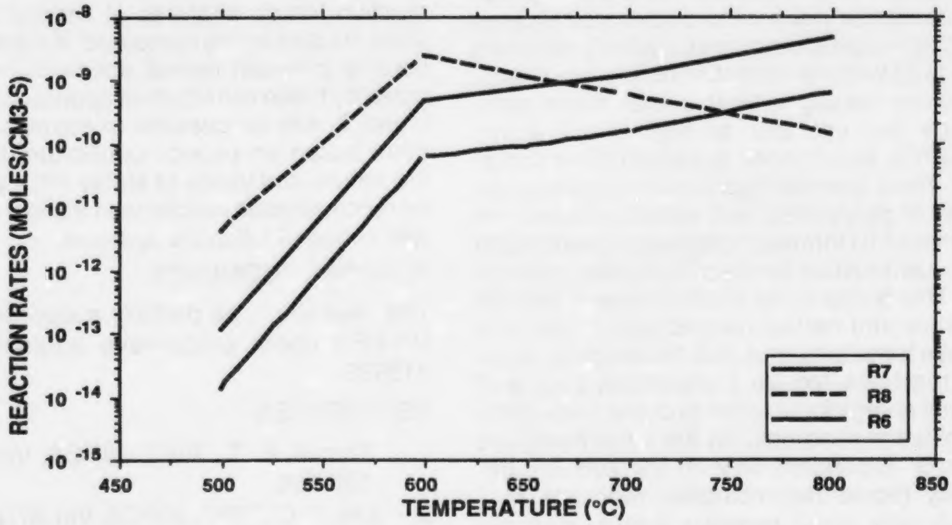

Figure 4. Comparison of reaction rates of C_2Cl_6 consumption from CCl_4 thermal decomposition. See Table 2 for a description of the CCl_4 decompostion mechanism and rate parameters.

rate of trichlorovinyl (C_2Cl_3) radical addition to unsaturated species such as C_2Cl_4 may be rate-limiting. We have recently conducted Quantum RRK calculations [21] demonstrating that C_2Cl_3 addition to C_2Cl_4 producing C_4Cl_6 is much more rapid than the hydrocarbon reaction analogue at combustion temperatures. We are currently analyzing similar molecular growth reaction channels in an attempt to identify the mechanism(s) leading to chlorinated aromatics from simple chlorinated hydrocarbons.

The results of this analysis indicate that knowledge of the steady-state radical concentrations is an important parameter in determining the relative importance of various reaction pathways leading to PIC formation. For $CHCl_3$, radical recombination reactions dominate the formation of C_2Cl_6 and C_2Cl_4 at lower temperatures and CCl_4 at higher temperatures. For CCl_4, recombination reactions are also responsible for C_2Cl_6 formation at low temperatures and the reformation of the parent compound at higher temperatures. For both mechanisms, radical-molecule reactions dominate the formation of C_2Cl_4 and higher molecular weight products at higher temperatures.

Full-scale testing of several hazardous waste incinerators and industrial boilers cofiring hazardous wastes indicate that chlorinated alkanes and chlorinated alkenes are frequently observed PICs [4,5]. With the exception of chloromethane, laboratory testing indicates that these compounds are unstable at high temperatures (> 900°C), even under oxygen-starved conditions. Thus, one may hypothesize that recombination of polyatomic and atomic species are important PIC formation pathways downstream of the combustion zones of full-scale combustors. This is due to the relative rates of radical-molecule and radical recombination reactions at these lower temperatures. Most radical-molecule reactions require a significant source of thermal energy for reaction to occur. Radical recombination reactions, on the other hand, are primarily dependent only on the collision frequency (some recombination reactions may exhibit very small negative temperature dependencies).

To reduce the concentration of PICs in the effluent of such systems, a modification of the waste feed composition, or a reduction in residence times at low temperatures may be effective PIC control strategies. A reduction in the Cl content of the waste or, more practically, thorough mixing of waste streams to remove high Cl pockets, should diminish the probability of formation of perchlorinated, polyatomic, reactive species in the high-temperature zones. Consequently, the probability of formation of high molecular weight perchlorinated species at high temperature will be reduced. Reformation of CCl_4 and other chlorinated alkanes at the exit of the high temperature zone will also be limited due to the low reactive species concentrations.

Numerical integration of the ordinary differential equations listed in Table 2 is currently being conducted to verify the importance of the aforementioned PIC formation pathways. In the near future, the high-temperature PIC formation mechanisms of other CHCs will also be evaluated in a similar manner. One of the objectives of these investigations is to determine the relative importance of radical-molecule and radical recombination reaction pathways leading to the formation of intermediate products. Concentrations of radical species from equilibrium and reaction kinetic analyses at various temperatures are also being compared. If a simple relationship between radical concentrations computed by these two different approaches can be found, it may be possible to develop an algorithm based on pseudo-equilibrium to predict the nature and yields of stable PICs produced by recombination reactions in the low temperature zones of full-scale systems.

ACKNOWLEDGMENTS

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Disclaimer

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COST EFFECTIVE REMEDIATION THROUGH VALUE ENGINEERING

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ABSTRACT

The recommended remedial action alternatives for a site, whether in the form of a Record of Decision (ROD) or consent order and agreement, allow a certain degree of flexibility in which several design options may be permissible as long as the intent of these decisions is maintained. A value engineering (VE) review allows the A/E to explore that flexibility. A VE review is a less time consuming and structured process than a formal VE study.

A VE review examines the major cost components of recommended alternatives to determine if:

- More cost-effective remedial actions can be employed, thus achieving the same level of remediation at a lower overall cost.
- The components of the remedial actions are adequate from an engineering and regulatory standpoint and, if not, what the cost impact of meeting these criteria would be.
- The costs presented in the ROD for specific alternatives are realistic and what the potential impact of a more accurate estimate might be.

This paper presents the advantages and disadvantages of VE reviews for environmental remedial design projects. Although VE reviews are routinely performed for government-lead remediation projects, they are not routinely used in the private sector. This paper, through examples, makes a case for more use in the private sector.

INTRODUCTION

The process by which the sites having environmental problems are remediated is somewhat complex and is contingent upon many variables. Principal variables are:

- Is the site on the National Priorities List (NPL)?
- Is the site being remediated in cooperation with or under the auspices of a regulatory agency?
- Is the remedial action the responsibility of a single entity or a group of entities acting in concert?

This paper explores the role of value engineering in determining cost effective remedial programs. A characteristic common to all remedial programs is that they tend to cost more than those funding the programs care to pay. A goal of all remedial action programs should be to provide maximum environmental benefit in terms of public health risk reduction, environmental impairment reduction, and future resource utility for the most reasonable cost. Remedial actions comprise a gammet of studies, technologies, and traditional design and construction practices.

Value engineering is hereby defined as the process by which one assesses the goals of a specific remedial action program, and in a very broad sense, evaluates and assesses a variety of approaches to fulfill those goals. Value engineering considers both capital costs and long-term costs associated with a variety of remedial approaches and provides a consistent presentation of cost information such that the appropriate decision makers for a given project are presented with the data necessary to select the optimal remedial alternative.

Value engineering sometimes results in studies to acquire data that is necessary for minimizing or even controlling overall project costs. Value engineering reviews are, in themselves, relatively inexpensive and tend to cost less than one percent of the overall project budget. Sometimes studies and design changes which result from value engineering reviews are significant in terms of their expenditures, however, these more expensive studies and assessments are only undertaken when the potential cost savings of the overall remedial effort are large in comparison to the cost of the study.

The following sections of this paper describe the remedial process for both NPL and non-NPL sites, and the value engineering process itself. This paper also presents two case histories of the adaptation of that value engineering process to real-world remedial programs and the resulting cost savings obtained via this process.

THE REMEDIAL PROCESS

Sites are assessed for cleanup through a variety of mechanisms. Many sites that have been placed on the NPL have been assessed and scored by the U.S. EPA and cooperating state agencies. Other sites have been placed on individual state priority lists and slated for cleanup under the auspices of the appropriate state agencies. Many cleanups come about as a result of a property transfer or simply an assessment performed on a voluntary basis by the owner or occupant of a given property. How the remedial process progresses is somewhat contingent upon who discovered the site, whether or not it is on the NPL, whether or not it is on a state priorities list, and whether or not a regulatory agency is involved in the process.

If a site is on the NPL, its remediation is normally accomplished through a process which involves a remedial investigation/feasibility study (RI/FS). During the RI/FS, the site is investigated and a series of alternatives, including a no-action alternative, are assessed from the standpoint of both public health risks and economics. The relative advantages and disadvantages of these alternatives are assessed in a manner that permits decision makers (normally the U.S. EPA Regional Administrator and staff members) to readily review environmental benefits achieved versus expenditures for a series of alternatives. This portion of the RI/FS process is actually quite analogous to a value engineering study, however, there is normally insufficient data available during the RI/FS process to assess in depth the specifics of design/remedial construction.

For sites that are not on the NPL, there is often no formal mechanism for assessing the environmental benefits achieved versus expenditures in the selection of the given remedial alternative. If a regulatory agency is involved in the remedial process for a non-NPL site, negotiations amongst the parties which will fund the study and the appropriate agencies are generally undertaken informally until a series of remedial actions are agreed upon or mandated.

For remediations which are not subject to regulatory scrutiny, the owner or other responsible party is in the position of making an assessment regarding the degree of risk reduction (environmental benefit), the amount of expenditures which may be employed, and often assess for themselves the measures most responsive to their individual needs. It is in this situation that a value engineering approach is oftentimes most beneficial, as owners or other responsible parties certainly have a vested interest in achieving: 1) a specified amount of environmental benefit/risk reduction at the least possible cost and/or, 2) achieving a maximum amount of environmental benefit/risk reduction at a given cost.

The points at which the value engineering process can be applied to the evaluation of remedial alternatives are a function of each project. The benefits of value engineering can be achieved at different points in the remedial planning process.

THE TRADITIONAL VALUE ENGINEERING PROCESS

The agency which is most familiar with the value engineering process is the U.S. Army Corps of Engineers. The Corps has traditionally applied value engineering concepts to both its design and construction projects throughout the past ten years. The traditional value engineering process is outlined in the U.S. Army Corps of Engineers' ENG Form 3986-R, dated September 1985. The process is described as a five-phase process consisting of the following:

- Phase I - Information Acquisition: In this phase, pertinent facts are established, the goals of the remedial process are clearly defined, the framework of the most likely remedial alternatives is established, and an appropriate team is assembled to perform the study. The key questions which are raised during this phase regarding each component of the series of alternatives identified are:

- What is it?
- What does it do?
- What must it do?
- What does it cost?

These questions are answered for the various components of the remedial alternatives in question and the information is recorded.

- Phase II - Critical Review: A group of individuals critically reviews the information recorded in Phase I. The techniques of this critical review are:

  - The use of creative thinking.
  - The elimination of regulations as a design constraint.
  - The elimination of unnecessary and redundant components.
  - The simplification of existing components and approaches.
  - The modification and combination of alternatives into a program or series of programs.

  Key techniques employed in this phase are:

  - The use of good human relations.
  - Not permitting the most vocal and outspoken person on the value engineering team to dominate conversation.
  - Requiring all participants to answer the following question for each alternative or component which has been established in Phase I: "What else will perform the basic functions?".

  Again, as in Phase I, the results of the discussions are recorded in a systematic manner.

- Phase III - Analysis: At this point, each series of remedial alternatives is criticized as an entity. Combinations of alternatives have been established and the advantages and disadvantages of those combinations are assessed in Phase III. The techniques which will be utilized are:

  - The use of realistic cost references.
  - Critical review of the ability of each series of alternatives to fulfill project goals.
  - Solicitation of an expert opinion outside the group, if necessary.

  The key questions to answer during Phase III analyses are:

  - What does each feasible series of alternatives cost, both on a capital basis and an O&M basis?
  - Will each series of alternatives realistically perform the project objectives, i.e., satisfaction of regulatory constraints, realization of true environmental benefit, etc.?

  During Phase III, we are assessing which alternatives will fulfill a basic level of project acceptability from a remedial standpoint and the cost of each of those alternatives.

- Phase IV - Critical Review: The best alternatives assessed in Phase III, in terms of cost effectively complying with project goals, are critiqued again using the following techniques:

- Specifics of each alternative are looked at in more detail in terms of design practicality and compliance with regulatory constraints.
- Evidence supporting the suitability of each series of alternatives is gathered and critically assessed, i.e., regulatory precedent, past project successes/failures, etc.
- Through refining the aspects of each series of remedial alternatives, modifications are made to the alternatives as though the value engineering team were spending its own money in performing the remedial program.

At end of Phase IV, after establishing the specifics of a series of remedial alternatives and evaluating how each series of alternatives may be employed as economically as possible, the key question to ask is; "Will these alternatives now meet all necessary project requirements?" This question should be answered in writing for each of the remaining alternatives at the conclusion of Phase IV.

- Phase V - Presentation: Phase V is a specific presentation, in writing, of the series of alternatives which have resulted from the previous four phases. This presentation is as follows:
  - Identification of the remedial program evaluated.
  - Brief summary of the problem.
  - Description of early impressions of the remedial alternatives.
  - Cost of original alternatives.
  - The results of the critical reviews of early phases on those alternatives.
  - Identification of alternative approaches.
  - Cost data associated with those approaches.
  - Advantages and disadvantages of each group of remedial alternatives.
  - Sketches of proposed approaches.
  - Problems and costs associated with implementation of each alternative.
  - Assessment of cost savings which could be realized by the implementation of alternatives.
  - A summary statement recommending the most appropriate alternative.

This process, as designed and often implemented by the U.S. Army Corps of Engineers, represents an innovative framework for assessing remedial alternatives. It was originally developed for non-remedial construction projects but has been employed by the Corps and by other parties in the assessment of environmental remediation projects.

CASE HISTORIES

The following case histories are the personal experiences of the authors and those of others in the authors' organization. These case histories highlight how the value engineering process, as previously described, was applied to specific environmental remediation programs and the resulting changes in remedial design and remedial construction from the process.

Case History No. 1

Case History No. 1 involves the remediation of an NPL site. The project was a federal lead project in which an RI/FS had been done in the early 1980s. The Record of Decision or selection of the most appropriate remedial alternative resulting from the RI/FS process was issued in early 1985. The proposed remedial alternative for the site included a variety of remedial techniques which included excavation and removal of highly-contaminated waste materials, retrofit of the groundwater/leachate collection and treatment system, a surface water management program, and a 26 acre cap for materials which were not highly contaminated and, based upon the Record of Decision, would remain in place.

One aspect of the Record of Decision was the specification of the type of cap which would be used to prevent surface water and precipitation from infiltrating into solid waste and municipal refuse. Based upon the data evaluated during the RI/FS process, which did indeed look at the environmental benefit achieved versus, in a qualitative manner, the amount of environmental benefit and risk reduction achieved, a specific cap design had been put forth. This cap design, however, was not critically reviewed during the RI/FS process to the degree it would have been during a value engineering study. Individual components of the cap, with respect to their ability to fulfill project objectives versus their capital and O&M costs, were not assessed in significant detail. During the remedial design process, a remedial design contractor was asked to perform an overall value engineering study using the techniques previously described.

During the design process the actual configuration of the capping system as well as the individual materials used in the capping system were assessed. During this review, additional data was solicited on the cost of the various materials for the design as specified in the Record of Decision. Cost and performance characteristics were also solicited for alternative materials and configurations which had the ability to fulfill performance objectives as well as or better than the materials selected and identified in the Record of Decision.

As a result of this value engineering review, it became apparent that the substitution of a synthetic geomembrane for a two-foot thick clay cap component, as depicted in the Record of Decision, had both performance advantages as well as significant potential cost savings. It was therefore recommended that the plans and specifications for this project be prepared with provisions for both a clay capping system and a geomembrane capping system and that the construction contractors be required to provide quotes on both alternatives.

Upon receipt of the competitive bids for the overall remedial program, all eight bidders indicated that they would install the synthetic capping system at a lower price than the capping system stated in the Record of Decision. The low bidder on the project had a price for the synthetic capping system which was $790,000 less than the capping system depicted in the Record of Decision.

The project was awarded with the government selecting the alternative of the synthetic capping system. Actual savings to the government for construction are $790,000. The actual cost of undertaking the overall value engineering study, specific portions of the value engineering study related to capping system components, and the preparation of an alternative design specifications and bid sheet was less than $50,000. Net savings to the government are approximately $740,000.

Case History No. 2

At another NPL site, the Record of Decision mandated that a leachate trench be constructed around the periphery of a land disposal area. The basis of this Record of Decision included data indicating groundwater contamination in the vicinity of the landfill, which was to be controlled, collected, and treated as part of the remedial action process. The perimeter collection trench was defined as an alternative and its estimated depth was based upon several monitoring wells constructed in the vicinity of the landfill. These monitoring wells indicated that groundwater impacts had indeed occurred at the landfill periphery. These wells, however, were constructed as open-hole monitoring wells, which at some points extended to a depth in excess of 70 feet. In addition, it was apparent that these wells intersected several hydrogeologic zones such that samples from these wells were actually a mixture of groundwater from several zones. The relative contribution of these zones to the contamination was impossible to determine.

During remedial design, problems were encountered with the Record of Decision collection option. Simply implementing the Record of Decision without critical review would have resulted in leachate collection/groundwater collection trenches being installed at depths of up to 70 feet around the periphery of this landfill, and that the installation be performed through 50 feet of hard rock at some points. Capital costs associated with the installation of this system are significant, the techniques for rock excavation are somewhat limited due to the desirability of not furthering fractures in the bedrock system.

During an initial value engineering review, performed in accordance with the techniques described previously, it was noted that the Record of Decision recommended collection trenches to a depth of approximately 70 feet based upon data obtained from monitoring wells at that depth. However, it had not been established that the contamination extended to a depth of 70 feet. The manner in which the monitoring wells were constructed made it impossible to determine with any degree of precision the hydrogeologic zones which actually exhibited contamination.

It was, therefore, recommended that the existing monitoring wells be properly abandoned and that they be replaced by wells that monitor discrete hydrogeologic zones such that the vertical extent of contamination could properly be assessed. A rational assessment of the vertical extent of contamination was imperative in properly designing a groundwater/leachate collection trench that would fulfill the goals of this project.

A subsurface investigation program and monitoring well installation program are currently in progress involving the installation of wells at certain critical locations which will be capable of obtaining samples from vertically discrete hydrogeologic zones such that the vertical extent of contamination can properly be evaluated. Should this program indicate that the preponderance of contamination is actually from zones substantially more shallow than 70 feet, as is currently believed, a remedial design will be undertaken which will have a leachate collection/groundwater collection system that is substantially more shallow than 70 feet and may in fact be constructed primarily in soil as opposed to rock. Should this approach be justified through the investigative programs currently underway, potential construction savings are approximately $2.7 million. The cost of performing these investigations and undertaking these studies is $92,000. The potential cost savings are obviously highly significant with respect to the expenditures incurred to gather this information.

SUMMARY

Using value engineering techniques, as originally developed, fostered and propagated by the U.S. Army Corps of Engineers, remedial planners are afforded the opportunity to achieve highly-significant cost savings with relatively limited expenditures. Two case studies have been presented in which the sum total of savings approach $3.5 million and the sum total of expenditures to achieve those savings is less than $140,000.

It is not the intent of this paper to indicate that the value engineering process in itself is a panacea regarding cost effective remedial planning. However, based upon real-world experiences at real-world sites achieved in the last three years, the potential for significant cost savings has indeed been demonstrated. These savings could be accomplished both at sites on which little regulatory involvement is anticipated up to and including NPL sites for which the Record of Decision has already been signed. The rational engineering design and remedial planning process provides ample opportunities for the incorporation of value engineering techniques at a variety of points in the remedial planning process, from initial project conception through remedial construction and implementation.

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THE IMPORTANCE OF EXPOSURE PATHWAYS IN TOXIC SUBSTANCE CONTROL: A CASE STUDY FOR TCE AND RELATED CHEMICALS

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ABSTRACT

Most current studies for the transport and sorption of toxic contaminants have focused on chemical, physical, and biological activity in the saturated zone of groundwater systems. However, volatile pollutants that can readily move between the aqueous and vapor phases in saturated and unsaturated zones have made the prediction of their fate and transport very difficult. In the soil environment, some categories of groundwater pollutants are recognized as biotransformable and/or biodegradable. Risk assessment on such a family of chemicals has not been thoroughly studied, except for some individual members of the family. In this paper exposure pathway analysis and its impact on risk assessment for a whole chemical family will be treated.

Various computer models for pollutant transport and transformation in the multimedia environment have been investigated with particular emphasis on the groundwater system. An exposure pathway analysis based on multimedia environmental transport models is developed, and will be used for risk assessment/management. A case study of Tricloroethene (TCE) and its related chemicals (in a biotransformable sense) has been conducted. The GEOTOX, FEMWASTE, and BIO1D computer codes have been used for the transport and biodegradation calculations so as to determine the environmental concentrations, the most important exposure pathways and a subsequent health risk assessment. Several interesting findings have been explored and will be presented in this paper.

INTRODUCTION

The growing concern with potential problems posed by toxic substances in the environment has led to pollution control legislation at the state and federal level. Such regulation should be based on assessment of the relative risks associated with emission and the costs of controlling them. Because of the complexity of the environmental transport/transform mechanisms regarding the emission of toxic substances, the determination of control costs as well as the assessment of health risks are generally difficult and are highly uncertain.

Toxic pollutants, when released to the environment, are distributed among environmental media (the air, water, and soil), and subsequently enter the human body through various exposure pathways. The potential health effects of these contaminants will depend on the dose received as a result of the exposure. In order to assess the risk, a thorough understanding of how the contaminants behave in various media and their possible pathways to humans is necessary.

TCE and related chemicals (in a biotransformable sense) such as vinyl chloride(VC), perchloroethylene(PCE), and 1,1-dichloroethylene(DCE) were selected for the present study because PCE and TCE are major industrial solvents used for degreasing metal parts and electronic components. They are among the most common volatile organic compounds(VOCs) detected in groundwater and reported all over the world.

PURPOSE

A framework for risk assessment regarding toxic wastes is being developed by the risk assessment group at UCLA with support from the National Science Foundation Engineering, Research Center. Research underway has as its focus, the improvement and development of options for toxic waste control and methods for their evaluation. One objective of the risk assessment group is to develop models and methods to address exposure pathways. The methodology being developed is applied to an exposure assessment of trichloroethylene(TCE) and its related chemicals. The case study represents a 'typical' situation and demonstrates the developed methodology. The results of this study can then be used as a risk management tool to provide information concerning site remediation.

APPROACH

Risk Assessment

In general, prediction of the following is necessary in order to assess the risks due to toxic wastes:

a) Chemical and physical state of the source, its rate of release and its magnitude.

b) Dispersion of the pollutant from the source in air, ground water, and other media given the meteorologic and hydrogeologic conditions of site.

c) Assessment of pollutant exposure pathways, ultimate human uptake, and predicted health effects.

The risk assessment and risk management methodology being developed can be broken into three major parts:

1. Source/receptor (risk) assessment -- source and site characterization, selection of appropriate transport and transformation models in the multimedia environment, and development of exposure pathway and dose/response models for health risk assessment.

2. Option generation -- based on the source/receptor assessment and available technologies such as biodegradation, air stripping, pumping with hot patch, etc., recommend options for remediation, mitigation or interdiction.

3. Risk management -- use goal-driven criteria for ranking alternatives which includes uncertainty in models and data, probability of success of

the technologies being applied, and socio-economic and socio-political considerations.

A flow chart of the risk assessment/management process is depicted in Figure 1.

Exposure Pathways Analysis

In this paper the major tool used for exposure assessment is the GEOTOX code [1] which is based on simplified multimedia modeling. Therefore, a composite multimedia modeling approach, using independent single-medium models for each medium, couples inputs and outputs in order to provide the necessary interactions between models. For example, BIO1D [2] is used for the biodegradation calculation in the unsaturated zone, and FEMWASTE [3] is used for the transport calculation. This approach serves to validate the simplified models employed in the GEOTOX code. However, a large number of model parameters are required and often unavailable. A best-estimate method has been employed to resolve this problem. The resulting environmental concentrations are used to determine the most important exposure pathway based on rate calculations for each pathway (i.e. inhalation, dermal contact and ingestion).

There are eight compartments used in GEOTOX to model the environment. They are air, air particle, upper soil, lower soil, ground water, surface water, biota, and sediment. Exposure is expressed as the rate at which a quantity of material comes in contact with the human system and is estimated from various pathways based on daily intake per unit body weight averaged over the population. The general model is expressed as:

$$E = 1/70 \text{ SUM } I_i(t), \ i = 1, p$$

where E = child, adult, or lifetime exposure; p = number of pathways; I_i = the daily intake by pathway i. The exposure pathways considered in GEOTOX are inhalation, drinking water ingestion, biota ingestion, meat and dairy product ingestion, fish ingestion, soil ingestion, and dermal absorption. For simplicity, the exposure rate for each pathway is calculated by multiplying each exposure factor and the concerned environmental concentration(s). For example, the drinking water exposure rate is determined by groundwater and surface water pollutant concentrations and an exposure factor which relates the age group and averge daily water intake. More detailed information can be found in McKone's report [1].

A Case Study -- TCE and Its Related Chemicals

There are two situations of interest for PCE, TCE, DCE, and VC discharges from a hypothetical site located in the San Diego region. They are described as follows:

1) PCE and its bio-decayed daughter TCE are treated in a coupled sense. This means that they are related by a bio-decay relationship in the simulation.

2) PCE, TCE, DCE and VC are treated as separate chemicals, i.e. no bio-decay relation is considered.

A similar case study for TCE alone was conducted by Cohen and Ryan [4] for the prediction of environmental concentration. A six-compartment multimedia model was used to simulate transport behavior in the San Diego basin.

PCE, TCE, DCE and VC undergo anaerobic transformation [5, 6, 7] in the unsaturated soil water zone. The bio-decay relationships between each chemical compound and their bio-decay half-life are shown in Figure 2. The important physical and chemical properties of PCE, TCE, DCE and VC are listed in Table 1. Viruses are believed to be solely responsible for the biodegradation reactions. The distance viruses can travel, depending on the nature of the soil and other site-specific factors, was reported to be as far as 67m vertically and 408m horizontally from land application [8]. Thus, the media that should be considered are upper soil, lower soil, groundwater, and sediment. This family of biodecay product and its effect on exposure pathway and health risk is considered. Better information can then be provided for overall health risk assessment and management. Also, the environmental concentrations predicted by Cohen and Ryan and some field measurements [9, 10] are used to compare the results obtained using the GEOTOX simulation.

The environmental settings, shown in Table 2, are compatible with Cohen and Ryan's compartmental system for the purpose of easy comparison. The removal and transformation rates in some compartments for PCE, TCE, DCE and VC, based on a best-estimate approach are shown in Table 3 and 4 respectively. The San Diego region is assumed to be 400 km square. The atmospheric height and depth of the water are 700m and 10m respectively. The average temperature is taken as 20 degree C, the average humidity is 7.8e-6 kg/L, and the yearly average wind speed is 5 m/sec. The partition coefficients for PCE, TCE, DCE, and VC are summarized in Table 5. The source strength is chosen to be the same as that in Cohen and Ryan's work [4] in the air compartment, which is 1.54×10^{-9} mole /hour/m^3.

Our approach is to obtain preliminary estimates of exposure to TCE, PCE, DCE, and VC contaminants and will be easily adapted to site-specific assessments.

PROBLEMS ENCOUNTERED

When PCE or TCE undergoes anaerobic biodegradation they will produce daughter products including various dichloroethene(1,1, 1,2 cis, 1,2 trans) and vinyl chloride which have been known as possible carcinogenic agents (probable human carcinogen [11, 12]). To simulate their behavior in the environment, each daughter product requires the solution of an additional equation where the decay sink of the parent chemical equation provides a source term in the daughter product equation. However, in reality it is possible for PCE, TCE, DCE, and VC to metabolize in biota and transform to other toxic products [13]. This leads to a higher removal rate in biota and a compounding effect on exposure and health impacts. Such a metabolic enhancement of removal of contaminants can be modeled if the metabolic rate constants are estimated correctly. Also, in the event of rain, scavenging will have a significant effect on the concentration in the upper soil and surface water compartments especially when a significant emission of TCE, DCE, or PCE occurs. A further investigation of these issues will be conducted in the near-term.

Vapor phase diffusion and sorption of the common volatile pollutant TCE, has been studied by Marrin [14] and Peterson [15]. However, inclusion of gas phase transport has not been found in the available multimedia transport codes. Also, one known deficiency in the GEOTOX model is its simplified modeling of intermedia transport processes of non-particulate pollutants. A proper correction of this problem and the ignored pathway will be investigated. Guidelines for modification of the existing computer code will be provided in the continuation of present research.

RESULTS

The results of the simulation in terms of environmental concentration and exposure rates are presented in Tables 6 through 8 for two simulated situations. The environmental concentrations of TCE predicted by GEOTOX with and without considering the effect of biodecay are compared to Cohen and Ryan's results and other studies Table 6. A comparison of exposure rates with and without considering biodecay for adult, child and lifetime average are shown in Tables 7 and 8. To compare relative exposure and ranking, the reference safe dose corresponding to a lifetime risk of 1 in a million is used. The relative ranking for PCE, TCE, DCE, and VC is shown in Figure 3.

Discussion

The environmental concentrations predicted by the GEOTOX code have less than an order magnitude deviation from field measurement as listed in Table 6. Clearly, further refinement of each compartment model will require more studies of intermedia mass transport processes and multimedia field data.

As a result of this study, we conclude that vapor transfer of PCE, TCE, DCE, and VC in various media such as upper soil, surface water, lower soil, and ground water are the most important transport routes. This is due to their high Henry's law constant which accounts for higher mobility in the vapor phase and a strong tendency towards the air compartment. In the exposure analysis, we found that drinking water exposure rate is lower for PCE(one order of magnitude) and TCE(two orders of magnitude) when biodegradation is considered. As for DCE and VC, there is little change for both cases. Inhalation and ingestion of contaminated drinking water and food are the principal routes for all chemicals under consideration, which partially coincide with a previous study by EPA [11, 12]. Biodegradation has only a secondary effect on exposure rate and health risk for medium and high Henry's law constant chemicals, as can be seen from Table 7 and 8. To properly assess the risk due to low Henry's law constant chemicals such as pesticides, it is necessary to consider biodegradation to more toxic chemicals.

The aid of various computer programs including BIO1D, GEOTOX, and FEMWASTE has made the prediction of the exposure rate and subsequent health impact possible. These programs are useful tools for the study of exposure pathways. They can provide critical information for applying remediation, mitigation or interdiction measures and can be used as a basis for the selection of dose-response models in subsequent risk assessments.

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Disclaimer

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Table 1: Physical Properties of PCE, TCE, DCE, and VC

Chemicals	PCE	TCE	DCE	VC
Physical Properties				
molecular weight	165.83	131.4	96.94	62.5
Henry's law const (torr/(mole/l)	17240	8837	99840	17610
organic carbon part. coef. k_{oc}	220.52	42.45	70.53	13.04
diffusion coef. in air (m^2/s)	7.0×10^{-6}	7.78×10^{-6}	9.94×10^{-6}	1.07×10^{-5}
difussion coef. in water (m^2/s)	8.834×10^{-10}	9.71×10^{-10}	1.09×10^{-9}	1.25×10^{-9}
bioconcentration factor	124.8	37.45	54.28	15.81

Note:

1. bioconcentration factor is defined as:

   bcf = (ppm in fish meat)/(ppm water).

2. air diffusion coefficient is calculated by Hirschelder formula at 25 degree C [16].
3. water diffusion coefficient is obtained from Wilke and Chang's work [17].

Table 2: Environmental Settings

Landscape : San Diego Ecoregion
area in km^2: 400
height of the air compartment (m): 700
humidity (kg/L): $7.8x10^{-6}$
wet deposition scavenging efficiency: 0.8
yearly average wind speed (m/s): 5.0
precipitation onto land (cm/yr): 72.2
precipitation onto surface water (cm/yr): 0.76
total surface water runoff (cm/yr): 3.0
land surface runoff (cm/yr): 2.3
atmospheric dust load (micro-gm/m^3): 61.5
deposition velocity of atmospheric particles (m/d): 334
evapotranspiration from soil (cm/yr): 41.9
evaporation from surface water (cm/yr): 1.17
thickness of the A soil horizon (m): 0.26
bulk density of the soil in the A horizon (kg/L): 1.3
water content of the soil in the A horizon (kg/L): 0.45
volumetric air content in the A horizon (L/L): 0.03
mechanical erosion rate (kg/km^2/yr): $3.06x10^5$
irrigation from ground water (cm/yr): 1.0
thickness of the B soil horizon (m): 2.4
water content of the soil in the B horizon (kg/L): 0.28
bulk density of the soil in the B horizon (kg/L): 2.0
volumetric air content in the B horizon (L/L): 0.02
groundwater inventory (kg/km^2): 2.1e09
porosity of rock in the ground water zone (L/L): 0.3
density of rock in the ground water zone (kg/L): 2.33
fraction of the total surface area in surface water: 0.015
average depth of surface waters (m): 6.0
suspended sediment load in surface water (kg/L): 0.0034
deposition rate of suspended sediment (kg/m^2/yr): 150.0
thickness of the sediment layer (m): 0.05
bulk density of the sediment layer (kg/L): 1.5
porosity of the sediment zone: 0.2
resuspension rate from the sediment layer (kg/m^2/yr): 150
ambient environmental temperature (k): 293
biota dry mass inventory (kg/km^2): $3.1x10^7$
biota dry mass production (kg/km^2/yr): $1.6x10^6$
biota dry mass fraction: 0.33
boundary layer thickness at air/soil interface (m): 0.02
boundary layer thickness at water/air interface (m): 0.02
boundary layer thickness at sediment/water interface (m): 0.02
fraction organic carbon in the upper soil zone: 0.024
fraction organic carbon in the lower soil zone: 0.001
fraction organic carbon in the groundwater zone: 0.00287
fraction organic carbon in the sediment zone: 0.02

Table 3: Removal Rates of PCE, TCE, DCE, and VC

Chemical Compartment	PCE	TCE	DCE	VC
air	$2.40x10^{-1}$	$2.40x10^{-1}$	$4.48x10^{-1}$	$3.38x10^{-1}$
air particle	$1.00x10^{-4}$	$1.00x10^{-4}$	$4.48x10^{-2}$	$3.38x10^{-2}$
upper soil	$2.94x10^{-2}$	$1.610x10^{-2}$	$1.307x10^{-2}$	$1.0x10^{-7}$
lower soil	$2.04x10^{-4}$	$1.61x10^{-4}$	$1.307x10^{-2}$	$1.0x10^{-7}$
ground water	$2.93x10^{-3}$	$1.610x10^{-3}$	$1.307x10^{-2}$	$1.0x10^{-7}$
surface water	$5.48x10^{-3}$	$8.33x10^{-2}$	$8.67x10^{-3}$	$8.66x10^{-3}$
sediment	$2.944x10^{-2}$	$1.610x10^{-2}$	$1.307x10^{-2}$	$8.66x10^{-6}$

Note:

Removal rate constants (1/day)

Table 4: Transform Rates of PCE, TCE, and DCE

Chemical Compartment	PCE	TCE	DCE
upper soil	$2.94x10^{-2}$	$1.610x10^{-2}$	$1.307x10^{-2}$
lower soil	$1.22x10^{-4}$	$1.61x10^{-3}$	$1.307x10^{-3}$
ground water	$2.93x10^{-3}$	$1.610x10^{-5}$	$1.307x10^{-4}$
sediment	$2.94x10^{-2}$	$1.610x10^{-2}$	$1.307x10^{-2}$

Note:

Transform rate constants (1/day).

Table 5: Partition Coefficients of PCE, TCE, DCE, and VC

Chemicals Compartment Interface	PCE	TCE	DCE	VC
Air/Water	0.09429	0.04833	5.461	0.9632
Soil1/Water	5.292	1.019	1.693	0.313
Soil2/Water	0.2205	0.0425	0.0705	0.01304
Rock/Ground water	0.06328	0.01218	0.02024	0.00374
Sediment/Surface water	5.954	1.146	1.904	0.352
Biota/Soil1	0.9448	4.9088	2.954	0.16
Meat fat/Diet	0.0094	0.0051	0.00318	0.00845
Milk fat/Diet	0.0094	0.0051	0.00318	0.00845
Fish/Water	124.8	37.45	54.28	15.81

Note:

1. Temperature is 293 degree K.
2. SOIL1 -- upper soil.
3. SOIL2 -- lower soil.

Table 6: Comparison of Environmental Concentrations of TCE

Compartment	GEOTOX*	GEOTOX**	COHEN & RYAN	LIVERPOOL	LA JOLLA
AIR	1.558×10^{-4}	1.556×10^{-4}	10^{-2}	6.4×10^{-3}	7.8×10^{-3}
PMAIR	2.86×10^{-13}	2.858×10^{-13}	/	/	/
BIOTA	2.29×10^{-2}	2.289×10^{-2}	/	/	/
SOIL1	4.670×10^{-3}	4.663×10^{-3}	4×10^{-2}	/	/
SOIL2	1.171×10^{-5}	1.697×10^{-3}	/	/	/
GWTR	1.57×10^{-5}	4.553×10^{-3}	/	/	/
SWTR	4.023×10^{-4}	2.611×10^{-2}	6×10^{-2}	3.3×10^{-1}	7×10^{-2}
SDMT	3.078×10^{-3}	2.912×10^{-2}	7×10^{-2}	/	/

Note:

1. * considering biodecay effect
2. ** no biodecay effect
3. PMAIR -- air particle
   SOIL1 -- upper soil
   SOIL2 -- lower soil
   GWTR -- ground water
   SWTR -- surface water
   SDMT -- sediment.

Table 7: Exposure Rates(/w Biodegradation)

Chemical: PCE

Pathway	adult exposure (mg/kg-d)	child exposure (mg/kg-d)	lifetime average (mg/kg-d)
Inhalation	9.62E-02	1.80E-01	1.08E-01
Drinking Water	6.60E-05	1.36E-04	7.60E-05
Biota ingestion	3.74E-05	1.78E-04	5.75E-05
Meat/dairy ingstn	3.34E-05	6.75E-05	3.83E-05
Fish ingestion	2.68E-05	3.39E-06	2.34E-05
Soil ingestion	2.23E-08	1.58E-07	4.17E-08
Dermal absorption	1.65E-08	6.48E-08	2.34E-08
Total	9.64E-02	1.81E-01	1.08E-01

Chemical: TCE

Pathway	adult exposure (mg/kg-d)	child exposure (mg/kg-d)	lifetime average (mg/kg-d)
Inhalation	4.90E-02	9.16E-02	5.51E-02
Drinking Water	5.97E-06	1.23E-05	6.88E-06
Biota ingestion	4.26E-05	2.02E-04	6.54E-05
Meat/dairy ingstn	9.30E-06	1.88E-05	1.07E-05
Fish ingestion	6.99E-07	8.86E-08	6.12E-07
Soil ingestion	3.86E-09	2.74E-08	7.22E-09
Dermal absorption	2.86E-09	1.12E-08	4.06E-09
Total	4.90E-02	9.19E-02	5.52E-02

Chemical: DCE

Pathway	adult exposure (mg/kg-d)	child exposure (mg/kg-d)	lifetime average (mg/kg-d)
Inhalation	1.16E-02	2.18E-02	1.31E-02
Drinking Water	4.26E-06	8.78E-06	4.91E-06
Biota ingestion	8.58E-07	4.08E-06	1.32E-06
Meat/dairy ingstn	1.35E-06	2.73E-06	1.55E-06
Fish ingestion	3.83E-07	4.85E-08	3.35E-07
Soil ingestion	1.36E-10	9.69E-10	2.55E-10
Dermal absorption	1.01E-10	3.97E-10	1.44E-10
Total	1.16E-02	2.18E-02	1.31E-02

Chemical: VC

Pathway	adult exposure (mg/kg-d)	child exposure (mg/kg-d)	lifetime average (mg/kg-d)
Inhalation	3.21E-01	6.01E-01	3.61E-01
Drinking Water	3.28E-04	6.75E-04	3.77E-04
Biota ingestion	1.80E-04	8.57E-04	2.77E-04
Meat/dairy ingstn	1.01E-04	2.03E-04	1.15E-04
Fish ingestion	7.88E-06	9.99E-07	6.90E-06
Soil ingestion	3.11E-09	2.21E-08	5.83E-09
Dermal absorption	2.31E-09	9.06E-09	3.27E-09
Total	3.22E-01	6.02E-01	3.62E-01

Table 8: Exposure Rate(/wo Biodegradation)

Chemical: PCE

Pathway	adult exposure (mg/kg-d)	child exposure (mg/kg-d)	lifetime average (mg/kg-d)
Inhalation	9.63E-02	1.80E-01	1.08E-01
Drinking Water	4.89E-04	1.01E-03	5.63E-04
Biota ingestion	3.75E-05	1.78E-04	5.76E-05
Meat/dairy ingstn	3.41E-05	6.89E-05	3.91E-05
Fish ingestion	1.70E-04	2.15E-05	1.49E-04
Soil ingestion	2.23E-08	1.58E-07	4.17E-08
Dermal absorption	1.65E-08	6.49E-08	2.34E-08
Total	9.71E-02	1.82E-01	1.09E-01

Chemical: TCE

Pathway	adult exposure (mg/kg-d)	child exposure (mg/kg-d)	lifetime average (mg/kg-d)
Inhalation	4.89E-02	9.15E-02	5.50E-02
Drinking Water	4.38E-04	9.02E-04	5.04E-04
Biota ingestion	4.25E-05	2.02E-04	6.53E-05
Meat/dairy ingstn	9.65E-06	1.95E-05	1.11E-05
Fish ingestion	4.54E-05	5.75E-06	3.97E-05
Soil ingestion	3.85E-09	2.73E-08	7.21E-09
Dermal absorption	2.86E-09	1.12E-08	4.05E-09
Total	4.94E-02	9.27E-02	5.56E-02

Chemical: DCE

Pathway	adult exposure (mg/kg-d)	child exposure (mg/kg-d)	lifetime average (mg/kg-d)
Inhalation	1.16E-02	2.17E-02	1.31E-02
Drinking Water	8.68E-06	1.79E-05	9.99E-06
Biota ingestion	8.57E-07	4.07E-06	1.32E-06
Meat/dairy ingstn	1.36E-06	2.74E-06	1.55E-06
Fish ingestion	1.30E-06	1.65E-07	1.14E-06
Soil ingestion	1.36E-10	9.68E-10	2.55E-10
Dermal absorption	1.01E-10	3.97E-10	1.43E-10
Total	1.16E-02	2.18E-02	1.31E-02

Chemical: VC

Pathway	adult exposure (mg/kg-d)	child exposure (mg/kg-d)	lifetime average (mg/kg-d)
Inhalation	3.21E-01	6.01E-01	3.61E-01
Drinking Water	3.24E-04	6.67E-04	3.73E-04
Biota ingestion	1.80E-04	8.57E-04	2.77E-04
Meat/dairy ingstn	1.01E-04	2.03E-04	1.15E-04
Fish ingestion	7.84E-06	9.93E-07	6.86E-06
Soil ingestion	3.11E-09	2.21E-08	5.83E-09
Dermal absorption	2.31E-09	9.06E-09	3.27E-09
Total	3.21E-01	6.02E-01	3.62E-01

Figure 1: Risk Assessment/Management Flow Chart

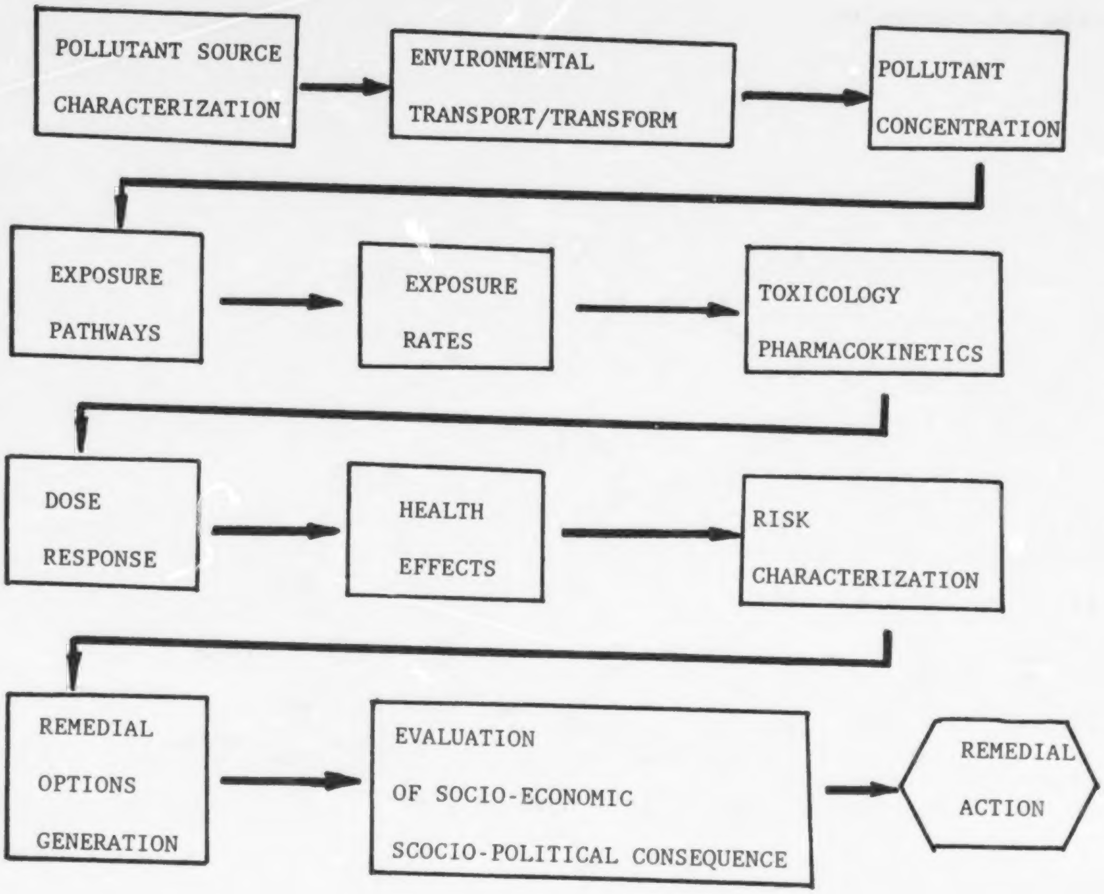

POLLUTANT SOURCE CHARACTERIZATION
ENVIRONMENTAL TRANSPORT/TRANSFORM
POLLUTANT CONCENTRATION
EXPOSURE PATHWAYS
EXPOSURE RATES
TOXICOLOGY PHARMACOKINETICS
DOSE RESPONSE
HEALTH EFFECTS
RISK CHARACTERIZATION
REMEDIAL OPTIONS GENERATION
EVALUATION OF SOCIO-ECONOMIC SCOCIO-POLITICAL CONSEQUENCE
REMEDIAL ACTION

Figure 2: Biodecay Relationship

Reductive Dehalogenation:

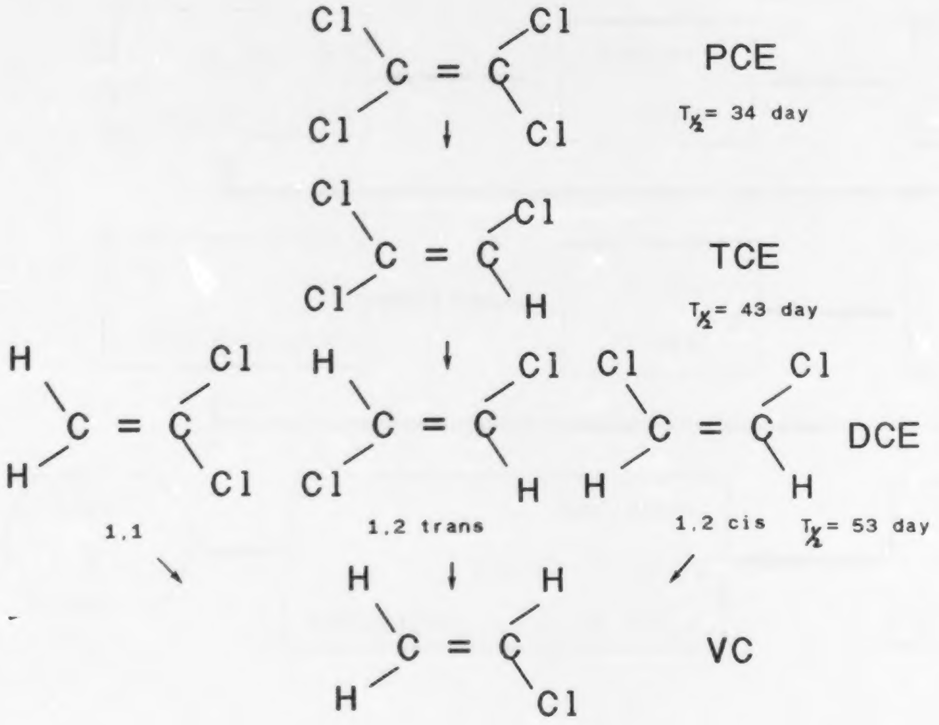
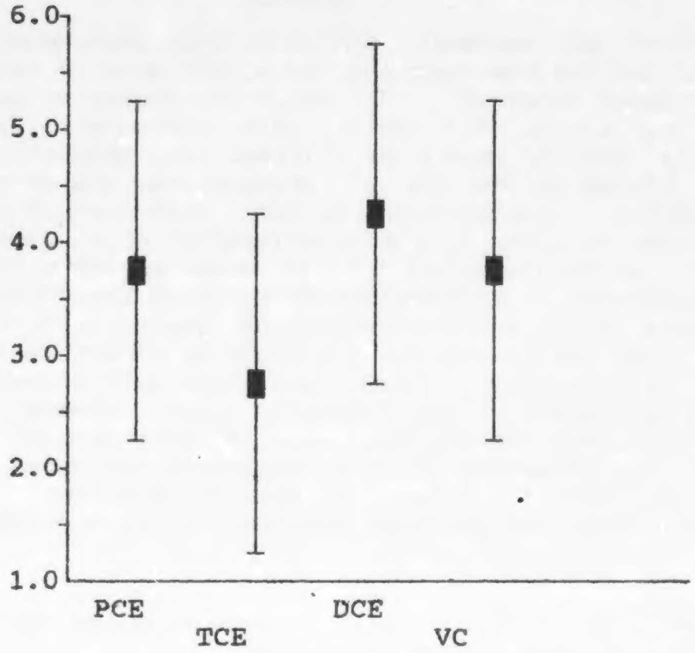

PCE
$T_{1/2}$= 34 day
TCE
$T_{1/2}$= 43 day
DCE
1,1
1,2 trans
1,2 cis
$T_{1/2}$= 53 day
VC

Figure 3: Relative Ranking of PCE, TCE, DCE, and VC



INTERNATIONAL PERSPECTIVES ON CLEANUP STANDARDS FOR CONTAMINATED LAND

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ABSTRACT

A critical but extremely difficult task associated with cleanup of contaminated land has been assessing the significance of contamination and the degree of cleanup required. To assist the Norwegian goverrment with its newly evolving program for dealing with contaminated land, a study was undertaken to identify approaches utilized internationally. A key part of this study focused on the use of predetermined standards, guidelines and criteria (PSGCs). This approach has been controversial and criticized for various reasons including lack of consideration of site-specific factors and insufficient (eco)toxicological data to establish PSGCs for a comprehensive list of contaminants. Nevertheless it was found that PSGCs are viewed as an important part of an overall program for dealing with contaminated land. There is a clear desire and need for PSGCs to streamline the assessment and cleanup of non-catastrophic sites, facilitate soil protection programs and encourage redevelopment of old industrial sites. However, it is recognized that PSGCs will not obviate the need for consideration of site specific factors nor risk assessment and risk management approaches. PSGC approaches have been utilized for years in several countries, most notably The Netherlands. Other nations have developed or are considering similar PSGC approaches.

INTRODUCTION

Norway has long been regarded as a pristine nation with majestic mountains and enchanting fjords. Unfortunately, during the past few years an increasing number of old waste sites and parcels of contaminated land have been discovered. For example, an old waste site was recently discovered near Oslo during railroad-related construction activities. The site had been used for dumping and burning of flammable liquids in an effort to reduce fires at a municipal landfill. Approximately 10,000 m^3 of soil contaminated with solvents ultimately were excavated and properly disposed of.

Since Norway derives most (> 80%) of its potable water from surface water, concern over ground water pollution has so far been limited. However, there is recognition of potential hazards to public health and the environment via other pathways. While there is little question that contaminated sites exist in Norway, little is known about the nature and extent of the problem. National inventories have recently been initiated including industrial branch surveys and old waste site surveys.

Discoveries of abandoned waste sites and contaminated land, often related to construction activities, have necessitated prompt action by regulatory authorities. As in the rest of the world, a critical but extremely difficult task has been assessing the significance of contamination at a particular site and determining the extent of cleanup required.

PURPOSE

A study was undertaken to identify the approaches used for establishing cleanup goals for contaminated land and the technologies employed to achieve those goals. The information derived was to assist the Norwegian government in the development and implementation of a newly evolving program for assessment and cleanup of contaminated land. A key aspect of this study concerned the perspectives toward and current application of "predetermined standards, guidelines and criteria" (PSGCs). A synopsis of this aspect of the work is given below while details may be found elsewhere [1].

APPROACH

Information for this work was gathered by several means. The international literature was surveyed by computerized and manual techniques. Personal inquiries were made to responsible agencies and individuals in ten countries with both well-established and relatively new programs for dealing with contaminated land (United States, Canada, England, The Netherlands, West Germany, France, Denmark, Sweden, Finland and Norway). Personal site visits were made where appropriate and feasible to gather firsthand information. The information gathered from all sources was reviewed and summarized.

PROBLEMS ENCOUNTERED

At the onset, the subject of this study was recognized as a complex one, intertwined not only with government policies and programs for dealing with contaminated land, but also with those for environmental protection in general. It was accepted that efforts to gather and review all relevant literature and contact all knowledgeable agencies and individuals would be futile. Rather attempts were made to gather representative current information. This was made somewhat difficult, since the issue of cleanup standards is a diverse and dynamic one on a local and national level, even in nations with apparently well established programs (e.g. USA, The Netherlands, West Germany).

RESULTS

Contaminated Land Programs

There are many different names used to refer to what might generally be defined as "contaminated land", but few formal definitions exist. Perhaps the most widely held is that put forth by NATO/CCMS [2]:

> *"Land that contains substances that, when present in sufficient quantity or concentrations are likely to cause harm directly or indirectly to humans, the environment or on occasions to other targets."*

Approaches to dealing with contaminated land have generally evolved in response to both industrial site redevelopment as well as improper waste management. In most cases, one or more notorious incidents has stimulated public attention and inquiry eventually leading to an awareness of the nature and extent of the problem. In response, legislation and regulations were enacted and policies and programs evolved. Some nations embarked on cleanup campaigns almost a decade ago (e.g. USA, The Netherlands) while others have begun in earnest only recently (e.g. Norway, France, Canada). The level of concern and program development may be related to many factors including population density, industrialization and reliance on ground water for drinking water (Table 1). In some nations the programs have been incorporated into broad soil protection programs. The clearest example of this is The Netherlands where powerful national laws were enacted in 1983 and 1987 (The Soil Protection Act) [3,4]. West Germany initiated a conceptually similar program in 1985 [5].

The nature and extent of the problem with contaminated sites varies widely between different nations (Table 2). Typically as concern grows, national inventories are initiated and cleanup programs are formalized. While the number of sites identified can be large, the number remediated and restored to productive use can be relatively small (i.e. typically <10%).

Early remediation efforts typically involved excavation and offsite treatment or landfilling. More recently there has been increased interest in onsite and in situ technologies such as vapor extraction, leaching and bioremediation. The situation in The Netherlands is somewhat unique in that there have been for years, numerous plants dedicated solely to treatment of contaminated soil. There are thermal, extraction and biological treatment plants with a total annual capacity of nearly 0.5 million m^3 [6]. Similar plants have been or are being implemented elsewhere (e.g. Denmark, Germany).

Approaches to Establishing Cleanup Goals

The approaches used to establish cleanup goals vary widely both within and between countries (Table 3). In a critical review of the USA Superfund program, the U.S. Office of Technology Assessment identified seven different approaches [7]: (1) ad hoc, (2) site-specific risk assessment, (3) national goals for residual chemicals, (4) cleanup to background or pristine levels, (5) best available technology or best engineering judgment, (6) cost-benefit approach, and (7) site classification. While these approaches are based on practices in the USA, they represent fairly the state of practices internationally. Regardless of the approach utilized, it is clear that science and engineering are but one part of the picture, with site-by-site decision making often heavily influenced by economic, social and political forces.

There has been considerable, sometimes heated, debate over which approach to establishing cleanup goals is the "best approach" [e.g. 7-11]. One aspect of this debate has centered around the establishment and application of PSGCs. There are advantages and disadvantages to this approach as will be outlined later. Given first is a review of the current attitudes toward and use of PSGCs in several countries around the world.

Table 1. Area and population densities of selected nations [28].

Country	Population (millions)	Area (10^3 sq.mi.)	Population Density (capita/sq.mi.)	Urban Population (%)
USA	247.5	3640	68	79
Canada	25.3	3852	6.6	76
United Kingdom	56.6	94.2	601	92
Netherlands	14.7	15.8	931	88
W.Germany	60.2	96.0	627	86
France	55.8	220.7	253	77
Denmark	5.1	16.6	305	84
Sweden	8.4	173.7	48	85
Finland	5.0	130.1	38	61
Norway	4.2	125.2	34	80
Statistic Date	1989	-	-	1980-1986

Table 2. General characteristics of "contaminated land".

	Site Discoveries	Site Remediation		
Country	Site Number and Concern	App. # Sites	Example Methods Commonly Used	ref.
USA	23000 ('87) with 900 ('87) nat. priority (NPL) sites.	130 NPL ?Non-NPL	Excavation/landfill Incineration Insitu treatment	7,8
Canada	Total unknown.	Few	Excavation/landfill	9
England	300 estimated.	>500	Isolation/capping Excavation/landfill	10,24
Netherlands	6060 ('86).	380	Excavation/treatment by thermal washing Excavation/landfill	6
West Germany	35000 ('85) with 5400 req. immediate action.	?	Encapsulation Excavation/landfill	18
France	453 ('87) with 82 serious.	95	Excavation/landfill Encapsulation Solidification	17
Denmark	1599 ('88). Estimate 9000 potential sites.	30-60	Excavation/landfill Incineration Onsite treatment	18,19
Sweden	3800 ('85) old waste sites with 500 est. of concern.	Few	Excavation/landfill Incineration Encapsulation	20
Finland	Total unknown. 1200 landfills with 378 with haz.wastes, 112 need immediate action.	Few	Excavation/landfill Some incineration Some landfarming	21
Norway	Total unknown.	Few	Excavation/landfill	22

Table 3. Approaches to establishing cleanup goals for contaminated land and use of predetermined standards, guidelines and criteria.

Country	Approaches to Establishing Cleanup Goals
USA	For NPL sites (i.e. Superfund) use applicable, relevant and appropriate federal and state requirements where available and formalized site-specific risk assessment methodologies. For non-NPL sites, procedures vary widely by State and government jurisdiction and include multiples of generic criteria and background levels as well as site-specific formalized risk assessment methodologies. [7-9,23]
Canada	Only Quebec has a formalized approach where a comprehensive list of generic criteria adapted from the "Dutch List" is used for initial guidance and screening with site-specific risk assessments as appropriate. [9,16]
England	No national system. National guidance on "Trigger Concentrations" for some contaminants commonly found on industrial sites commonly considered for redevelopment (e.g. old gas works). [10,24]
Netherlands	National policy of maintaining soil "multi-functionality". Generic criteria (A-B-C levels) for evaluating significance of pollution enacted in 1983 (often referred to as the "Dutch List". Reference values for good soil quality (new A-level) enacted in 1987. Contaminated land must be cleaned up to multi-functional quality (A-level) unless it is shown to be technically or financially unfeasible or environmentally harmful. [3,4,6,11-14]
West Germany	No national approach, control by provincial governments (Lander). Use of "Dutch List" with consideration given to local conditions. West German "Guides/Threshold" values for soil contamination now under development based on soil protection policy initiated in 1985. [5,18,25]
France	No national approach, control by local governments. Use qualitative risk assessments. If pollution by natural substances, must reference background. Development of standards for soil pollution now under consideration. [17,18]
Denmark	No national approach, control by local governments. Use "Dutch List" for general guidance and screening as well as existing Danish standards where available. Final decision on particular site based on site-specific considerations. Formalized risk assessment methods now under development. [19,26]
Sweden	No national approach. Limited experience to date. Use generic criteria (e.g. "Dutch List") if available for initial guidance but site specific decision based on local factors including technical, political, economic and psychological. [20]
Finland	No national approach. Limited experience to date. Use generic criteria (e.g. "Dutch List") for initial guidance. [21,27]
Norway	No national approach. Limited experience to date. Use generic criteria (e.g. "Dutch List") if available for initial guidance. Site-specific decision based on intended site use, technical feasibility and cost as well as secondary contamination during cleanup. [22]

Predetermined Standards, Guidelines and Criteria

The desire and need for PSGCs specific to contaminated land were evident in most of the ten countries considered. Readily available, comprehensive PSGCs were viewed as essential to facilitating initial site review and screening. There are demands for unequivocal cleanup criteria, often put forth by owners, developers and future users of contaminated land. Equally evident, however, was a strong appreciation for the difficulties and potential problems of establishing and implementing PSGCs and the belief that there must be site-by-site flexibility in setting final cleanup goals.

The first country to establish a national, comprehensive set of PSGCs for contaminated land was The Netherlands [3,11-13]. In 1983 a national act was promulgated which put forth the concept of "multi-functionality" for soil and included criteria for assessing the significance of soil and ground water contamination and guiding site assessment and cleanup ("Dutch List", Table 4)[3]. In support of a broad soil protection policy, reference values were recently enacted for a "good soil quality" [12]. All of these criteria were never intended to be standards, but rather guideline values for deciding upon the necessity for carrying out (further) investigations and risk assessments [3,14]. In practice however, the criteria have been implemented as if they were in fact standards, in parts of The Netherlands and elsewhere (Table 3). In 1988, the province of Quebec, Canada promulgated their own similarly comprehensive list of criteria, based in large part on the "Dutch List" [15].

Other national and provincial government agencies have also established PSGCs in the form of acceptable limits for soil contaminants. These have different names including "Trigger Concentrations" (England; Table 5), "Cleanup Guidelines" (New Jersey, USA; Table 6), and "Guide/Threshold Values" (West Germany). While far less comprehensive than the Dutch or Quebec lists, they are intended to serve as guidance in site assessment and cleanup. In many cases the criteria are given with reference to a proposed land use (e.g. Table 5). In most cases, the PSGCs are not legal standards, but rather guidance criteria intended to be used with due consideration of site specific factors. The exceptions seem to be for a few notorious substances such as polychlorinated biphenyls (PCBs), some polycyclic aromatic hydrocarbons (PAHs) and dioxins.

Even in those jurisdictions where PSGCs have not been formulated specifically for cleanup of contaminated land, reference is commonly made to existing PSGCs, such as the Dutch List (Table 3). There is also direct use or adaptation of existing national or international standards, often developed under programs and legislation unrelated to contaminated land. Examples include drinking water standards, ambient water quality standards, storm water runoff limits, limits on sewage sludge application to agricultural lands, occupational air quality standards, ambient air quality standards, and so forth. Notably, in several instances, ground water quality standards have been set roughly equivalent to drinking water standards (e.g. Wisconsin, USA, Denmark, The Netherlands). In some cases, reference to existing

Table 4. Soil and groundwater criteria used in The Netherlands for assessing the significance of contaminated land ("Dutch List") [3].[1]

Component	Soil (mg/kg dry matter)			Groundwater (ug/L)		
	A-Level	B-Level	C-Level	A-Level	B-Level	C-Level
1. Metals						
Chromium	100	250	800	20	50	200
Cobalt	20	50	300	20	50	200
Nickel	50	100	500	20	50	200
Copper	50	100	500	20	50	200
Zinc	200	500	3000	50	200	800
Arsenic	20	30	50	10	30	100
Molybdenum	10	40	200	5	20	100
Cadmium	1	5	20	1	2.5	10
Selenium	20	50	300	10	30	150
Barium	200	400	2000	50	100	500
Mercury	0.5	2	10	0.2	0.5	2
Lead	50	150	600	20	50	200
2. Inorganics						
NH4 (as N)	-	-	-	200	1000	3000
F (total)	200	400	2000	300	1200	4000
CN (tot.free)	1	10	100	5	30	100
(tot.comp.)	5	50	500	10	50	200
S (total)	2	20	200	10	100	300
Br (total)	20	50	300	100	500	2000
PO4 (as P)	-	-	-	50	200	700
3. Aromatic Compounds						
Benzene	0.01	0.5	5	0.2	1	5
Ethylbenzene	0.05	5	50	0.5	20	60
Toluene	0.05	3	30	0.5	15	50
Xylenes	0.05	5	50	0.5	20	60
Phenols	0.02	1	10	0.5	15	50
Total Aromatics	0.1	7	70	1	30	100
4. Polycyclic Hydrocarbons						
Naphthalene	0.1	5	50	0.2	7	30
Anthracene	0.1	10	100	0.1	2	10
Fenanthrene	0.1	10	100	0.1	2	10
Flouranthene	0.1	10	100	0.02	1	5
Pyrene	0.1	10	100	0.02	1	5
Benzo(a)pyrene	0.05	1	10	0.01	0.2	1
Total Polycyclics	1	20	200	0.2	10	40
5. Chlorinated Hydrocarbons						
Aliphatics (Ind.)	0.1	5	50	1	10	50
Aliphatics (Tot.)	0.1	7	70	1	15	70
Chlorobenzenes (Ind.)	0.05	1	10	0.02	0.5	2
Chlorobenzenes (Tot.)	0.05	2	20	0.02	1	5
Chlorophenols (Ind.)	0.01	0.5	5	0.01	0.3	1.5
Chlorophenols (Tot.)	0.01	1	10	0.01	0.5	2
Chlor. PAHs (Tot.)	0.05	1	10	0.01	0.2	1
PCBs (Tot.)	0.05	1	10	0.01	0.2	1
EOCl (Tot.)	0.1	8	80	1	15	70
6. Pesticides						
Chlor. org. (Ind.)	0.1	0.5	5	0.05	0.2	1
Chlor. org. (Tot.)	0.1	1	10	0.1	0.5	2
Pesticides (Tot.)	0.1	2	20	0.1	1	5
7. Other Pollutants						
Tetrahydrofuran	0.1	4	40	0.5	20	60
Pyridine	0.1	2	20	0.5	10	30
Tetrahydrothiofene	0.1	5	50	0.5	20	60
Cyclohexanone	0.1	6	60	0.5	15	50
Styrene	0.1	5	50	0.5	20	60
Fuel (gasoline)	20	100	800	10	40	150
Mineral Oil	100	1000	5000	20	200	600

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[1] These values are guidelines not "standards". A-level implies unpolluted, B-level implies pollution present and further investigation required, C-level implies significant pollution present and cleanup required (back to A-level).

Table 5. Tentative "Trigger Concentrations" used in England [24].[1]

Compound	Planned Land Uses	Trigger Concentrations	
		Threshold	Action
		(mg/kg air-dried soil)	
Selected Inorganic Contaminants			
Arsenic	Domestic gardens, allotments	10	To be developed
	Parks, playing fields open space	40	To be developed
Cadmium	Domestic gardens, allotments	3	To be developed
	Parks, playing fields open space	15	To be developed
Chromium (Hexavalent)	Domestic gardens, allotments	25	To be developed
	Parks, playing fields open space		
Chromium (Total)	Domestic gardens, allotments	600	To be developed
	Parks, playing fields open space	1000	To be developed
Lead	Domestic gardens, allotments	500	To be developed
	Parks, playing fields open space	2000	To be developed
Mercury	Domestic gardens, allotments	1	To be developed
	Parks, playing fields open space	20	To be developed
Selenium	Domestic gardens, allotments	3	To be developed
	Parks, playing fields open space	6	To be developed
Boron (wat.sol.)	Any uses where plants are grown	3	To be developed
Copper	Any uses where plants are grown	130	To be developed
Nickel	Any uses where plants are grown	70	To be developed
Zinc	Any uses where plants are grown	300	To be developed
Contaminants Associated with Former Coal Carbonization Sites			
Polyaromatic Hydrocarbons	Domestic gardens,allotments,play areas	50	500
	Landscapes, buildings, hardcovers	1000	10000
Phenols	Domestic gardens, allotments	5	200
	Landscapes, buildings, hardcovers	5	1000
Cyanide (free)	Domestic gardens,allotments,landscapes	25	500
	Buildings, hardcovers	100	500
Cyanide (comp.)	Domestic gardens, allotments	250	1000
	Landscapes	250	5000
	Buildings, hardcovers	250	None
Thiocynanate	All proposed uses	50	None
Sulphate	Domestic gardens,allotments,landscapes	2000	10000
	Buildings	2000	50000
	Hardcovers	2000	None
Sulphide	All proposed uses	250	1000
Sulphur	All proposed uses	5000	20000
Acidity (pH)	Domestic gardens,allotments,landscapes	5	3

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[1] All proposed values are tentative and/or preliminary requiring regular updating. All values are for concentrations determined on "spot" samples. If all values are below the threshold concentrations, site may be regarded as uncontaminated for these contaminants and development may proceed. Above the thresholds, remedial action may be needed. Above the action concentration, remedial action will be required or the form of development changed.

Table 6. Cleanup guidelines used in the State of New Jersey, USA [9].

Substance	Soil	Groundwater
	(ppm)	(ppb)
Chromium	100	50
Zinc	350	-
Lead	100	50
Copper	170	-
Arsenic	20	50
Cadmium	3	10
Selenium	20	10
Nickel	100	-
Barium	-	1000
Mercury	-	2
Silver	-	50
Total Volatiles	1	-
Volatiles plus Base Neutrals	-	100
Total Hydrocarbons	100	-
Petroleum Hydrocarbons	100	1000

standards has been formally incorporated into a waste site cleanup program (e.g. USA Superfund program).

DISCUSSION

Based on the information derived in this study, it became apparent that there were numerous potential advantages and disadvantages of a PSGC approach to establishing cleanup goals (Table 7). Approaches employing PSGCs are not claimed to be the best approach for setting cleanup goals, but rather a necessary part of an overall program for dealing with contaminated land. PSGCs facilitate national or regional soil protection programs and encourage redevelopment efforts for contaminated land. In this context they may be used for both initial screening and contamination assessment as well as for determination of final cleanup goals. For contaminated sites of national and regional significance (e.g. uncontrolled hazardous waste sites involving large concentrations or amounts of highly toxic materials) such a PSGC approach will usually not be appropriate. While PSGCs may provide an early indication of the extent of the problem, site-specific risk assessments will likely be needed and risk management decisions will necessarily have to be made.

The use of PSGCs appears to be gaining favor in many nations, especially for use in preliminary assessment of the significance of contamination and the potential extent of cleanup. The Netherlands has used this approach for more than 5 years to remediate several hundred sites [6,13]. Recently, the Province of Quebec in Canada, issued a similarly comprehensive list of soil and ground water criteria, in large part adapted from the "Dutch List" [15]. Establishment of similar lists is also under consideration in other

Table 7. Example advantages and disadvantages to the use of predetermined cleanup standards, guidelines and criteria.

Advantages
- Speed and ease of implementation.
- Similar sites would be handled in a similar manner.
- Useful for initial assessment of significance of contamination.
- A priori information facilitates planning and action.
- Encourages developers to undertake decontamination and restoration.
- Potential consistency with strategies for environmental standards.
- Reality of contaminated land made easy for layman.
- Facilitate environmental audits of industrial sites.
- Facilitates monitoring/permitting of operational industrial sites.
- Can be used for performance assessments of soil treatment plants.
- Implies non-negotiability and reduces local political influences.

Disadvantages
- Some important site-specific considerations cannot be accounted for.
- Standards, guidelines and criteria are not formulated for many toxic substances of concern. Existing standards formulated under other programs are not necessarily appropriate for contaminated land.
- PSGCs imply a level of understanding, knowledge and confidence which likely does not exist.
- Once PSGCs are established, site-specific flexibility may be difficult.

jurisdictions (e.g. Alberta, Canada [9,16], West Germany [5], France [17]).

It appears that PSGCs represent an important component of an overall program to deal with soil protection and contaminated land. The challenge is to develop scientifically well-founded PSGCs specific to contaminated land which are consistent with other laws and regulations and supported by various concerned parties (e.g. scientific and engineering community, regulators and politicians, environmental and citizens groups).

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THE STATUS OF HAZARDOUS WASTE MANAGEMENT IN TAIWAN, R.O.C.

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ABSTRACT

A large quantity of industrial waste is produced daily in Taiwan, R.O.C.. A 1985 survey found that the amount of waste generated equalled approximately 30 million tons per year. Hazardous waste represents 9.7% of this total. Based on statistics from this same 1985 survey, 72% of the factories disposed of their waste without intermediate treatment. Since most methods used for treatment of hazardous wastes were implemented incorrectly, the proper treatment of such waste has become the focal point of environmental protection in Taiwan. From July, 1987 the "short-term program for industrial waste control" has had as its first priority the control of toxic, infectious and corrosive hazardous waste. At the same time, a registration system for permission, reporting and results inspection for hazardous wastes is being developed. An industrial waste exchange and reclamation system is also being developed. It is predicted that a complete hazardous waste management program can be developed within the next four years.

INTRODUCTION

In the past forty years, owing to successful economic policies and the hard work of our people, Taiwan has experienced an economic miracle known as the "Taiwan Model". While our economic growth has won the praise of many countries, serious environmental pollution has been closely following the footsteps of economic development. A 1985 survey found industrial waste totalled approximately 30 million tons per year.(1) Hazardous waste represented 9.7% of this total. The survey investigated 1,600 factories which are potential sources of hazardous waste. Among them, 72% of the factories disposed of their waste without intermediate treatment. Table 1 shows present intermediate treatment methods for industrial waste. Table 2 & 3 indicate types and quantities of waste. 28.76% of waste was dumped in landfills, 52.15% was recycled and reused, 13.91% was not disposed of (ie. it was stored, etc.), 0.02% was dumped into the ocean and the method of handling 4.98% was unknown. The majority of businesses in Taiwan are small or medium size companies. These companies have difficulty handling their hazardous waste. They can not afford the huge investments required to build facilities and would have trouble finding trained professionals to operate facilities if they had them. Laying responsibility for hazardous waste treatment on the individual company is not a realistic approach. Therefore, building an effective hazardous waste control program, solving emergent hazardous waste issues, constructing waste treatment facilities and planning a waste exchange system are our current emphases.

Table 1. Present intermediate treatment methods for industrial waste in Taiwan.

Method	Percentage %
Physical treatment	4.03
Chemical treatment	5.68
Biological treatment	0.75
Incineration	8.03
Other thermal treatment	1.03
Others	7.87
Untreated	72.33

PURPOSE

An Amendment to the Waste Disposal Act was approved in November 1985 in an effort to solve the hazardous waste problem and prevent toxic chemicals from contaminating the environment. Two years later, a high level Environmental Committee was organized by coordinating several divisions of the central government. A four year "short-term program for industrial waste control" has been developed.(1) It projects four goals from July 1987 to June 1991.

1. Give highest priority to toxic, corrosive, and infectious industrial waste. 2. Set up a record-reporting and self-monitoring system for industries to control main pollution sources. 3. Build hazardous waste treatment facilities and disposal sites to prevent illegal dumping. 4. Plan and promote the waste exchange and reuse systems.

APPROACHES

We have studied our own unique environmental problems as well as similar problems experienced by industrialized countries, such as the U.S., Japan, and several European countries, in order to draw guidelines for our environmental programs. Several criteria have been included to manage hazardous waste effectively. They are:

1. A solid legal basis. 2. Allowance standards for environmental pollution. 3. Equipment for data processing, monitoring and composition analysis. 4. Permit procedures for storage, treatment and disposal(TSD)facilities. 5. Effective facilities and management system. 6. Sufficient personnel and funds. 7. Promotion of waste minimization strategies such as: the recycling and reuse of industrial waste, improvements in the manufacturing process, and waste exchange.

According to the above considerations, we are planning to implement the following control measures:

Control Program:

Four systems have been introduced to regulate industries and hazardous waste treatment organizations. They are: a permit-recording system, a planning-permission system, a recording system, and an inspection system. Figure 1 shows the framework of these control systems. All information gathered in these systems is incorporated into a Chemical Substance Management System in order to help build a nationwide network of information useful in the handling and prevention of chemical disasters.

Table 2. Eighteen Catagories for Industrial Waste. Data taken form survey of 1623 factories. Note that each factory may have several different types of waste.

Waste Type	Industrial Waste		Hazardous Waste	
	No. of factories	Average Monthly Volume	No. of factories	Average Monthly Volume
		Tons month-factory		Tons month-factory
ash	78	24.10	63	28.16
concentrated dust	137	38	115	35.68
metal slag	507	5.72	476	5.90
mineral slag	43	88.12	39	94.27
process slag	92	130.50	71	40.24
sludge from wastewater treatment	364	57.69	292	67.31
oil/water mixture	66	47.17	60	51.87
waste oil	57	1.89	48	2.18
waste acids	147	38.86	136	38.78
waste base	82	35.83	72	35.05
waste container	323	11.11	295	11.01
waste paper	446	2.72	312	1.95
waste solvent	151	8.80	131	8.52
refinery slag	49	37.86	23	4.70
waste plastics	242	3.22	178	3.53
waste rubber	47	1.14	37	1.07
waste fiber	66	21.93	50	24.23
others	611	8.28	503	8.18
Total	1623	45.15	1462	36.93

Table 3. Volume of toxic industrial waste in Taiwan

Toxic substance	No. of factories	Waste volume Tons/Month/factory	Percentage %
Hg	26	2.62	0.01
Cr	88	7.87	1.03
Pb	109	4.69	0.70
As	6	3.13	0.04
Cd	25	43.89	1.61
Zn	194	10.10	3.00
Cu	527	6.30	5.07
Cyanide compound	28	8.70	0.37
Fluorinated compound	25	11.74	0.45
PCBs	2	0.0001	-
Org-P compound	72	30.47	3.21
Org-Cl compound	131	2.95	0.46
Metal & Metal compound	503	18.46	14.18
Other organic	1702	26.22	69.78

Hazardous Waste Treatment Facilities:

Because most companies on Taiwan do not have huge investments or the technical know-how required to build hazardous waste treatment facilities, the government will first set up such facilities to act as models. The government will also provide incentives to encourage private companies to move into the hazardous waste treatment business. The EPA and the Industrial Development Bureau (IDB), (under the Ministry of Economic Affairs) are coordinating companies located inside industrial parks in building waste treatment facilities within those parks. Since the treatment facilities will be located within the parks where waste is produced, the cost and risk of transporting waste for treatment will be reduced. It is also expected that locating the treatment facilities in the industrial parks will be more acceptable to a public loathe to have such facilities "in their back yard". In addition, EPA and IDB are coordinating companies which produce similar kinds of hazardous waste in cooperating with each other by, for example, jointly funding the construction of their own treatment facilities.

Decreasing the Effect of High Impact Hazardous Waste on the Environment:

Several years ago, a hazard to human health arose when rice-bran oil was contaminated by Polychlorinated biphenyls (PCBs). Most recently, a Cadmium-rice accident was caused by industrial effluent containing cadmium flowing into rice fields. These accidents caused a great wound to our society and there are still other potential wastes threatening the public health. It is estimated Taiwan has 1000 tons of PCBs, 2000 tons of the Cd-sludge and 120,000 tons of mercury-containing sludge. These dangerous pollutants are the first priority of our work. In addition, we are planning to incinerate infectious waste on a regional basis. Treatment of infectious hospital waste is our first target.

Promoting Waste Minimization Stratagies:

Our short-term targets are the recycling and reuse of large amounts of waste, including: pesticide containers, waste oil, rubber tires, solvent, and plastics. Information on waste will be published periodically. Data on the quantity and quality of waste will be provided to industries to promote recycling and reuse.

Other control measures we are actively on include:

1. Developing legislation. 2. Establishing an information databank. 3. Promoting information exchange among government divisions. 4. Carrying out research and development. 5. Promoting education and training programs.

PROBLEMS ENCOUNTERED

The inherent complex property of hazardous waste pollution forms a difficulty challenge for us. Hazardous waste has various forms, is distributed widely, and huge quantities are generated at a high rate. Proper treatment demands a tremendous amount of investment as well as technological know-how. The following issues are encountered in the process of hazardous waste control:

Insufficent Regulations:

Before 1985 there was only the Waste Disposal Act to regulate the treatment of solid waste, but the contents of the Act were over simplified. The Act only required that a plant must take care of the treatment of its own waste. This act did not regulate treatment facilities or specify control measures. Regulations relating to hazardous waste were nonexistent. It was not until 1985 that the the Waste Disposal Act was amended to include the regulation of hazardous waste.

Lack of Accurate Data on Hazardous Waste:

We conducted a survey of hazardous waste in 1985, however the actual amount of hazardous, waste is still unclear. There are approxiately 80,000 factories in the Taiwan area. Complete data about their waste and treatment methods is still unavailable. Tables 2 & 3 show the results of the 1985 survey, roughly indicating the different kinds and amounts of hazardous waste in Taiwan. Without sufficient information, nationwide planning for hazardous waste control is handicapped. The Industrial Technology Research Institute is presently working on a more comprehensive nationwide survey.

Adequate Treatment and Storage Facilities are Unavailable in Both the Public and Private Sector

The progress of environmental protection in the ROC is similiar to that of other industrialized countries. In the early stages, only waste water and air pollution issues were addressed. Hazardous waste was not a major concern, resulting in a shortage of treatment facilities.

Shortage of Skilled Personnels and Funds:

The Environmental Protection Bureau, the forerunner of the present EPA, was not a cabinet level department in the central government. At the time of its existence, the public did not have a good sense of environmental protection. As a result, there was a serious shortage of manpower and funds for environment protection in both the central and local governments. The management of hazardous waste involves a high degree of scientific knowledge, specially trained professionals and a tremendous amount of investment. It was not until August 22, 1987 that the formation of the EPA brought with it a huge increase in the amount of finances and personnel for environmental protection.

RESULTS

In August 22, 1987 the Environmental Protection Administration (EPA) was organized, with Dr. Eugene Chien as administrator. Since then, environmental protection has moved into a new era. The number of personnel has increased from 124 in the Environmental Protection Bureau era to 284; the budget has increased from US$164.7 million (1987) to US$ 11.7 million (1989). US$ 2.4 million has been invested for hazardous waste control in 1989 and US$ 37 million is estimated to be invested in 1990. Since the implementation of the "short-term program for industrial waste control" we have achieved the following:

Legislation

We are actively formulating and amending laws in order to build a sound foundation for environmental protection affairs. The new Waste Disposal Act includes: the definition of and standards for hazardous waste; different treatment procedures for solid and hazardous waste; regulations for the import and export of toxic substances, etc. Standards for hazardous waste are listed in Table 4. We have several newly proposed regulations based on the Waste Disposal Act. These regulations govern: the storage, cleaning and treatment of industrial wastes; facility standards; public and private waste disposal organizations; the setting up of industrial waste treatment facilities; the certification of public and private waste disposal technicians; and the incineration and landfill-dumping of hazardous waste.

Control System

The EPA has declared that hazardous waste is the top priority of this year's work. The framework for waste control, as presented in Figure 1, has already been organized. We have set aside as top priorities for special improvement and monitoring programs fourteen industries: the smelter, oil-refinery, petrochemical, dye and its intermediate substances, Ti02 and related products, asbestoes, coal & related products, metal surface treatment, textile, tannery, waste recovery, nickel, cadmium, lead and mercury battery, acid-alkaline, pesticide, and environmental pesticide industries. Laboratory and hospital waste have become additional targets recently. Table 4 lists the extraction test limits for hazardous waste.

Treatment Centers

The EPA is planning to set up waste treatment demonstration centers in northern and southern Taiwan. (2) Planning stages have been completed and funds for the first phase of the project have been obtained from the 1987 and 1990 fiscal year budgets. A treatment center for the concentrated solution of electroplating is being planned and is expected to be in operation by June 1990.(3) The Waste Disposal Act allows the organization of private waste teatment businesses, treatment facilities, landfills or any qualified TSD facilities. Several companies have already planned to move into the field.

Recycling and Reuse

The Industrial Technology Research Institute organized the first Waste Exchange Information Center (WEIC) in November 1987.(4) WEIC provides information on waste for companies which produce or use waste. Up to the present, 292 factories have registered their information, 486 exchange cases have been recorded and a total of 40,000 tons waste have been exchanged.

Table 4. Standards for hazardous waste extraction tests

Toxic chemical substance	Extractable Limit (mg/l)	Content %
Organic mercury	ND	-
Mercury	0.25	-
Lead	5.0	-
Cadmium	0.5	-
Chromium	10.0	-
Chromium (VI)	2.5	-
Copper	15.0	-
Zinc	25.0	-
Arsenic and arsenic compounds	2.5	-
Cyanide compounds	5.0	-
Pesticides		
1. organic phosphorus	2.5	-
2. carbarmate	2.5	-
3. organic chloride	0.5	-
2,3,7,8, tetrachloro dioxine	ND	-
Asbestos		15
Chlorinated solvents		1

REFERENCES

1. EPA, R.O.C., 1988, Short-term Control Measures of Hazardous Waste, EPA-043770030.

2. EPA, R.O.C., Report on the Planning of a Hazardous Waste Treatment Demonstration Facility, 1988, EPA-044770026.

3. Industrial Development Bureau, R.O.C., Planning of an Industrial Waste Treatment Facility, 1988, Unpublished.

4. Union Chemical Laboratory, Industrial Technology Research Institute, Waste Exchange Communication, 1987.

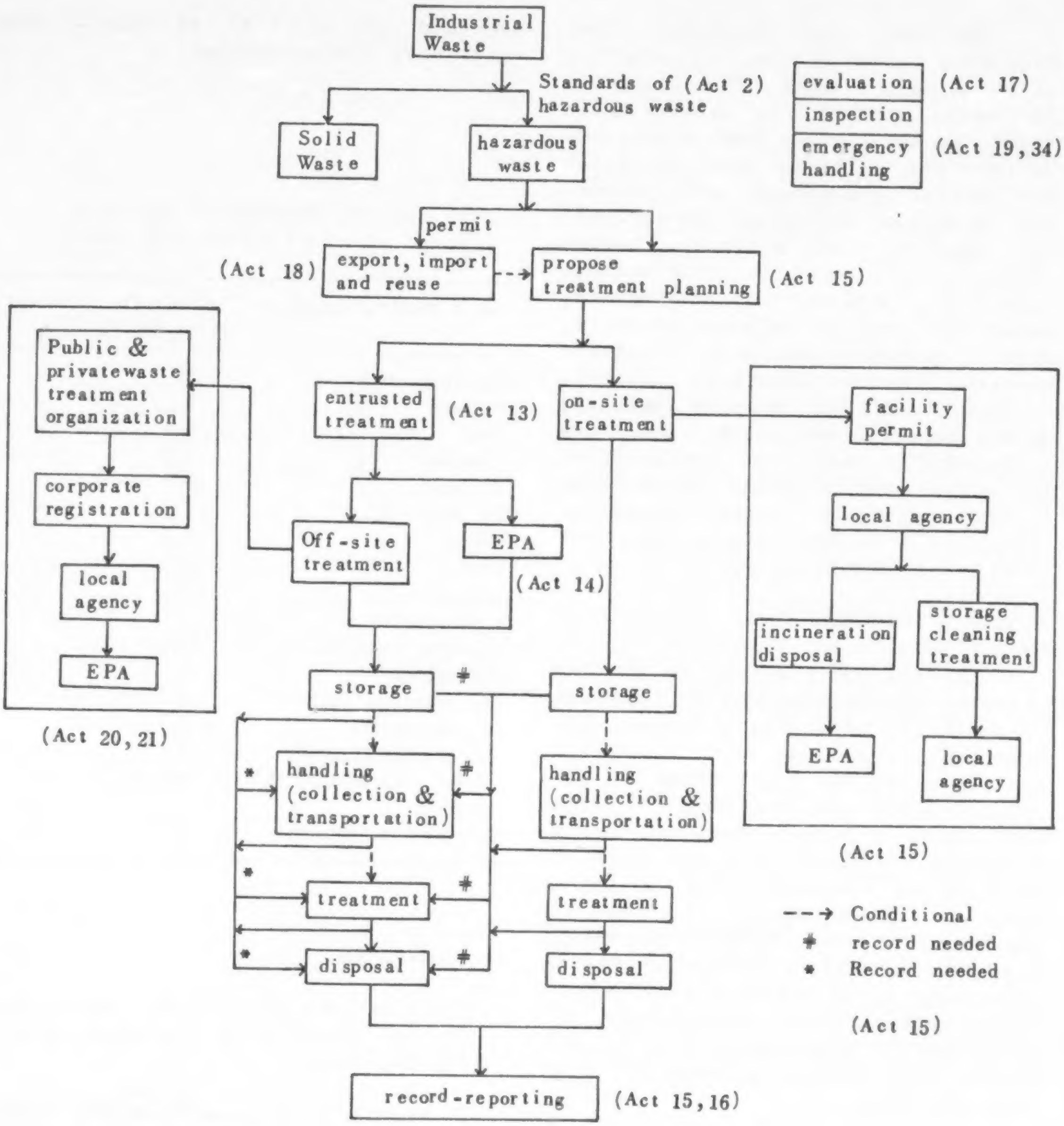
Industrial Waste
Standards of (Act 2) hazardous waste
Solid Waste
hazardous waste
evaluation
(Act 17)
inspection
emergency handling
(Act 19, 34)
permit
(Act 18)
export, import and reuse
propose treatment planning
(Act 15)
Public & private waste treatment organization
corporate registration
local agency
EPA
(Act 20, 21)
entrusted treatment
(Act 13)
on-site treatment
Off-site treatment
EPA
(Act 14)
facility permit
local agency
incineration disposal
storage cleaning treatment
EPA
local agency
(Act 15)
storage
#
storage
*
handling (collection & transportation)
#
handling (collection & transportation)
*
treatment
#
treatment
*
disposal
#
disposal
--→ Conditional
# record needed
* Record needed
(Act 15)
record-reporting
(Act 15, 16)

Figure 1 Framework of hazardous waste control program

CHEMICAL WASTE MANAGEMENT IN HONG KONG

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ABSTRACT

In Hong Kong, the control of chemical wastes is provided for in the Waste Disposal Ordinance. The enabling regulations of the Ordinance are presently being drafted and will be enforced in the near future. Presently, because of the lack of legislative control together with a general lack of knowledge on chemical wastes and the unavailability of suitable treatment facilities, the majority of the chemical wastes generated are being discharged into the sewers or drains. In order that the control regulations can function effectively, it is decided that a Chemical Waste Treatment Centre (CWTC) has to be provided by Government to ensure that the proper treatment facilities are available to the industry in the first place. As the majority of the chemical waste producers in Hong Kong are small generators, it is envisaged that most of these waste generators will have to rely on the CWTC for the proper treatment of their chemical wastes. The CWTC will also provide a waste collection service to collect and transport the chemical wastes from the industrial establishments to the CWTC. The waste generators are required to provide sufficient interim storage for their waste prior to their collection.

Because of the scarcity of land in Hong Kong, most of the small chemical waste generators are located in multi-storey industrial buildings on a shared occupancy basis. The storage space available in these small establishments is generally limited and is, as a rule, of second priority to production areas. The current study attempts to identify the potential problems that may arise due to the requirement for industries to provide interim storage of chemical wastes, and to provide a set of basic solutions to alleviate the problem.

INTRODUCTION

Over the past decade, the economy of Hong Kong has experienced tremendous growth. The GDP having risen by an average 10% per annum. This is largely due to the performance of its export-oriented manufacturing industry. As a result of the increased industrial activities, large quantities of chemicals are consumed, which, in turn, results in a large amount of chemical waste. Chemical wastes are also generated from non-manufacturing industries, mainly as residues from the storage of materials and damaged or unwanted products. According to a recent study commissioned by the Environmental Protection Department (EPD), about 100,000 tonnes of chemical wastes were generated in Hong Kong in 1987. These include waste acids, alkalis, etchants, toxic metals bearing wastes, organic solvents and oily wastes. Table 1 is a breakdown of the estimated waste arisings of the different types of chemical wastes (3).

In Hong Kong, the control over chemical wastes is provided in the Waste Disposal Ordinance. The enabling regulations of the Ordinance are presently being drafted and will be enforced in the near future, subject to the completion of the legislative procedures. Presently, because of the lack of legislative control coupled with a general lack of expert knowledge of chemical wastes and the lack of suitable treatment facilities, only a limited quantity of chemical wastes are disposed of by approved means, such as at a Government operated codisposal landfill or in house treatment plant. The majority of the chemical wastes are simply discharged into sewers or drains. In order that the proposed Waste Disposal (Chemical Waste) Regulations can function effectively, a Chemical Waste Treatment Centre (CWTC) will be provided by Government to ensure that the proper chemical waste treatment facilities are available in the first place for use by industry. As the majority of the chemical waste generators are small establishments, it is envisaged that most of the waste generators will have to rely on the CWTC to properly dispose of their wastes. It is intended that a design-construct-operate contract will be awarded to a consortium with world recognised expertise in the design, construction and operation of centralised chemical waste treatment facilities. The treatment facilities to be provided will include oil/water separation units, chemical/physical treatment units and a high-temperature incinerator. The contractor is also encouraged via the contract terms to establish material recovery units as optional additions to the CWTC. The CWTC operator will also provide a collection service to collect and transport chemical wastes from the waste producers' premises to the CWTC. The waste producers will be required to provide interim storage of their waste prior to the collection.

PURPOSE

As in many other cities the

majority of chemical waste producers in Hong Kong are small generators. An analysis of the size distribution of the potential waste generators indicated that about 85% of the industrial establishments employ less than 20 workers, and about 95% employ less than 50 workers(5). Available statistics (1) indicated that about 90% of the chemical wastes generators are located in multi-storey industrial buildings. According to a recent survey conducted by EPD on industrial buildings in the Kwai Shing area (a heavily industrialised district) (4), a typical multi-user industrial building could hold up to 680 factories, and the average floor areas per establishment could range from 25 to 2800 square meters. These waste producing establishments represent the majority of the chemical waste producers in Hong Kong. Storage areas are always secondary to production and storage of chemical wastes will be given an even lower priority. The safe storage of chemical wastes before their collection by the CWTC operator will be a difficult issue complicated by the requirement for the safe storage of incompatible chemical wastes.

The objective of the current study is to identify the potential problems that may arise during the operation of the CWTC in respect of the chemical waste storage in the waste producers' premises, so that practical solutions could be worked out beforehand to alleviate the situation.

APPROACH

There are about 50,000 industrial establishments in Hong Kong (2). Of these, about 11,500 industrial establishments are considered to be potential chemical waste generators. In order to accurately assess the potential problems that may arise when the Waste Disposal (Chemical Waste) Regulations are enforced and the chemical waste generators are forced to provide interim storage for their wastes, an industrial survey was commenced in summer 1988. The survey concentrated on a number of target industries that are considered to be potential chemical waste generators. These target industries include electroplating, electronic, fabricated metal, electrical machinery, transport equipment, non-ferrous metal products, spray painting and optical equipment.

The survey was conducted in the following manner:

Questionnaires were first sent to selected industrial establishments to inquire into their chemical waste generation pattern. Specific questions were included to probe into the practical problems related to waste storage. Follow up visits were then conducted to the selected establishments by appointment. During the site visits, the field officers conducted detailed inspection/interviews with the responsible personnel of the industrial establishments on the issue of chemical waste generation and present methods of disposal. Observations were made in respect of the ability of the establishment to provide interim storage of chemical wastes. In many case, the field officers had to assist the interviewees to accurately complete the questionnaire. In all cases, the field officer would go through the production processes with the interviewees to understand and identify the quality and quantity of the chemical waste streams. The information obtained were then analysed with a view to identify the potential problems associated with the interim storage of chemical wastes and the feasible solutions. Appendix 1 is a sample completed questionnaire from a typical electroplating factory.

PROBLEMS ENCOUNTERED

The questionnaire-visit approach was considered useful as it was noted that many of the interviewees had little knowledge on the chemical wastes they generated and their proper management. The follow up visit and the field officers' assistance in the completion of the questionnaire is considered vital in attaining accurate information for the subsequent analysis.

Another problem encountered was related to the availability of storage space. Most of the chemical waste generators are small establishments located in multi-storey industrial buildings where shared tenancy on the same floor is a common feature. The solutions proposed must be practical in terms of utilisation of space, affordable in terms of financial requirement, and acceptable in terms of the safety standpoint.

RESULT

So far, questionnaires were sent to a total of 87 industrial establishments, 74 questionnaires were returned or collected. Follow up visits were conducted to 37 establishments. Of the 37 establishments visited, 23 generated appreciable amount of chemical wastes. A number of the chemical waste generators, notably the printed circuit boards (PCB) manufacturers and the electroplators, generate more than one waste stream. Some of the wastes generated were found to be incompatible, such as cyanide waste and waste acids from a typical electroplating factory. In such cases, different waste containers, and, depending on the waste generation pattern, physically separated interim storage areas would be required.

A number of points were observed in the survey:

(a) Due to the shortage in factory space, storage areas were given very low priority in the utilisation of available area. In many cases, storage areas for chemicals constitute only about 0.5 to 3 percent of the total floor area. In some extreme cases, there were no "designated" storage area for chemicals in the factories at all. (see Plates 1 & 2). But much of the difficulty could be alleviated via better planning in terms of production processes and factory layout.

(b) In many cases, the chemical waste generators have little knowledge about the general properties of the raw chemicals that they are using (except, perhaps, for the role of the chemical in the production process), and even less so for the chemical wastes generated. It was noted that in many cases, different chemicals, some of which were incompatible, were seen stacked together at the same place. (see Plates 3 & 4). This observation calls for the need for an extensive programme to educate the chemical waste generators on the properties and hazards of chemical wastes (and chemicals) and the proper ways to manage these wastes. It also points to the need for comprehensive Codes of Practice on the proper methods to handle, store and dispose of chemical wastes. Also, any proposed solution for the interim storage problem has to be simple and straight forward in order that the waste generators can easily comply.

(c) The rate of chemical waste generation could be highly variable with respect to the type of industry as well as the actual production processes adopted in a particular factory. In most cases, only small quantities of chemical wastes are generated during the processes and the discharge frequency could be as low as once per half year (when the spent chemicals in a process bath are discharged). For PCB and electroplating factories, however, substantial quantities of different chemical wastes could be generated each day. The discharge rates and frequencies would have serious implications on the collection requirements for the CWTC operator as well as the interim storage requirements for the generators.

(d) Most of the establishments interviewed were unwilling to disclose financial information, but from the information gathered, the capital set up cost of a typical chemical waste generating small "flatted factory" (employing less than 20 operatives) could be in the range of 300 thousand to 6 million Hong Kong dollars (i.e. about 40 to 800 thousand US dollars). Assuming normal plant life of 7 years, the amortised capital cost would be in the range of 43 to 860 thousand Hong Kong dollars Per annum. Similarly, the available range of annual turnover rate is 1.9 to 9.6 million Hong Kong Dollars.

From the survey findings, EPD is in the process of designing a number of basic plans for the interim storage of chemical wastes for the reference of (small) chemical waste generators. In addition, general "collection plans" are being considered to provided guidance for the CWTC operator on the collection of the chemical wastes. It is considered that the recommendations should be :

(a) Simple, so that the waste generators can easily and accurately follow.

(b) Practical, so that the recommendations can be put into practice. Care should be taken to avoid onerous and financially unaffordable arrangements which could act as disincentive deterring waste generators from making use of the CWTC service to solve the chemical waste disposal problems.

(c) Notwithstanding (a) and (b), the recommendations must provide adequate safety in practice.

Considering the above constraints, it is recommended that :

(a) In all cases, waste generators should review carefully their existing production processes to identify opportunties for waste reduction or material recovery.

(b) The CWTC operator will provide the containers for the interim storage of chemical waste. This will ensure that only the correct types of containers are used. A reverse-milkman service should be provided in which the CWTC operator will collect chemical wastes from the factories at the required frequency while at the same time provide adequate empty containers for the interim storage of chemical wastes generated before the next collection.

(c) The waste generators will be required to provide simple interim storage for the chemical wastes-generated. No permanently constructed stores are specified but different types of wastes (especially incompatible wastes) should be stored separately. It is proposed that corrosive wastes or non-flammable toxic wastes should be stored in bunded areas with impermeable bunds and floor to avoid spillages and seepages. Impermeable floor areas can be created by chemical treatment of existing floor or the use of large drip trays made of appropriate materials grouted to the floor. For flammable wastes, free standing safety storage cabinets up to required safety specifications could be used if permanent stores are not available or impractical.

(d) To fully utilise the vertical headroom within the storage areas, purpose built multi-tier racks could be used for the storage of chemical wastes. For small generators, small waste containers such as 25-litre jerricans instead of the standard 200-litre drums are recommended for easier handling and better flexibility in stacking, and as a result reduce the area requirements. Case studies of typical multiple wastes generators (such as electroplating factories) adopting the above recommendations indicated that both the set up and the amortised cost for the installation of the above recommended storage arrangements are much less than HK$10,000 per annum - far less than their annual turnover rate.

(e) To ensure safe storage of the chemical wastes and the efficient operation of the CWTC, it is further recommended that maximum chemical waste storage limits should be set to limit the total quantities of different chemical wastes allowed to be stored in the industrial premises before collection. At the same time, a collection "trigger" level should be set. When the chemical waste under interim storage reaches the "trigger" level, the waste generator may call upon the CWTC operator to collect the waste. This will ensure that sufficient quantities of chemical waste are available at the time of collection while at the same time the chemical waste generators are responsible for providing an acceptable level of storage space for their wastes.

(f) All storage areas as well as the containers have to be properly labelled. Preferably, the containers should have colour codes to assist easy identification of their content.

It is envisaged that the above recommendations could form the basis of a series of practical but safe solutions to assist chemical waste generators to provide interim storage for their chemical wastes before their ultimate collection by the CWTC operator. In view of the wide variations in the industry types involved and their production practices, it is considered that the current survey should be further extended. At the same time, consultation and education programmes should be organised via meetings and Codes of Practice issued to the industrial sectors.

REFERENCE

(1) Anon. 1987a, directory of Hong Kong Industries, 1987, Hong Kong Productivity Council.

(2) Anon. 1987b, Names of Buildings 1987, Rating and Valuation Department, Hong Kong.

(3) Anon. 1988, Environment Hong Kong 1988 - A Review of 1987, Environmental Protection Department, Hong Kong.

(4) Chan, E., 1989, Industrial Survey of Kwai Shing in Kwai Tsing District, Environmental Protection Department, Hong Kong.

(5) Unpublished industrial survey data, Environmental Protection Department, Hong Kong.

Table 1 **CURRENT AND LIKELY FUTURE CHEMICAL WASTE ARISINGS**

Waste type	1987	1992	1997
Acid	20,000	22,000	25,000
Alkali	35,000	42,000	50,000
Copper containing waste solution	12,640	19,150	25,160
Zinc containing waste solution	13	13	14
Nickel containing waste solution	120	140	160
Other metal salts containing waste solution	1,200	1,300	1,400
Cyanide containing waste solution	100	130	160
Non-chromium bearing oxidizing agents	10	11	12
Chromium bearing oxidizing agents	55	59	68
Halogenated solvents	1,300	1,700	2,000
Non-halogenated solvents	1,500	1,800	2,100
Phenols and derivatives	2	2.2	2.4
Polymerization precursor and production wastes	40	42	44
Mineral oil	5,600	5,700	5,900
Fuel oil	50	51	53
Oil/water mixtures	12,000	13,000	13,000
Pharmaceutical products	1	1	1
Mixed organic compounds	130	140	150
Mixed inorganic compounds	70	74	78
Miscellaneous chemical wastes	30	32	35
Interceptor & Treatment Plant sludge	40	42	44
Tank cleaning sludge	1,000	1,000	1,000
Tar, asphalt, bitumen and pitch	140	143	146
Tannery wastes	400	400	400
Printing wastes	90	93	94
Dyestuff wastes	70	59	52
Plating bath sludge	10	11	12
Paint wastes	640	700	750
Waste catalysts	4	4	4
MARPOL Annex I (a)	5,000	N/A	N/A
MARPOL Annex II (b)	500	N/A	N/A
Total (rounded up)	98,000	110,000	130,000

(a) Oily wastes arising from the application of annex I of the International Convention for the Prevention of Pollution from Ships (MARPOL Convention).

(b) Chemical wastes arising from the application of Annex II of MARPOL Convention.

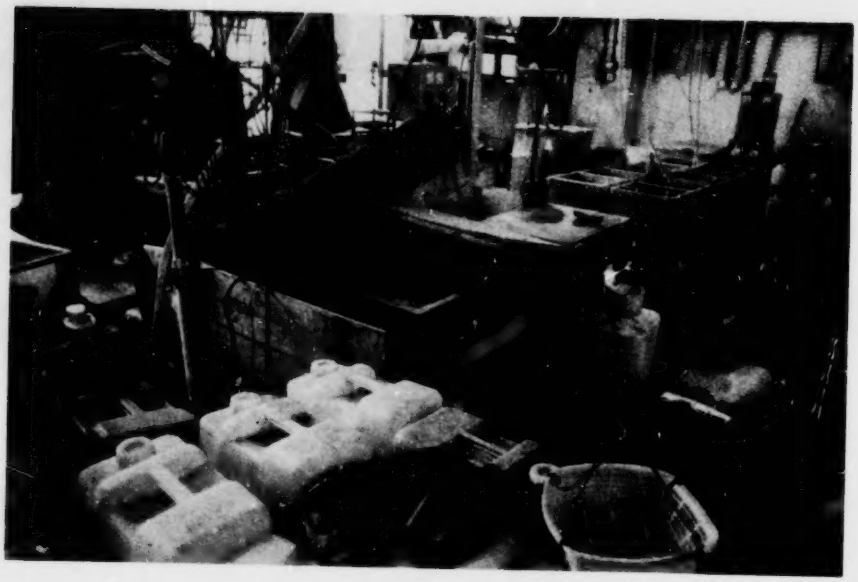


Plate 1 A Typical Small Scale Electroplating Factory in Hong Kong. (Note the Storage of Different Types of Chemicals in the Foreground)

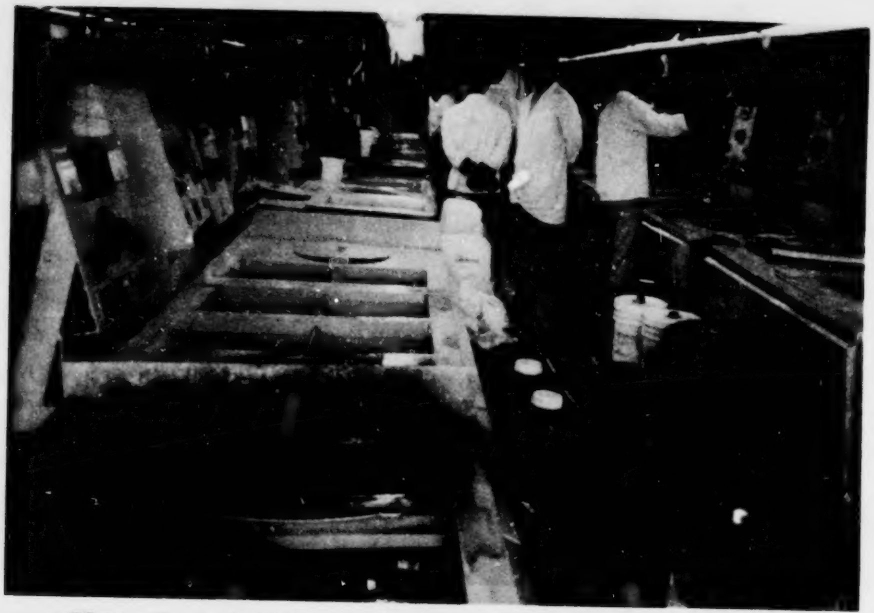


Plate 2 A Medium Scale Factory (Electroplating) (Note the Stacking of Chemicals along the Process Line)

Plate 3 Storage of Different Chemicals at the Same Place - A Typical Scene in Many Factories

Plate 4 Another Shot Showing the Storage of Different Chemicals at the Same Place. (Note the presence of Cyanide Containing Salt (the Green Drum) and Chromic Oxide (the Red Drums))

Appendix 1

公司概況

I. COMPANY PROFILE

公司稱號
Company Name : [redacted]

地址
Address :

電話
Tel No. :

聯絡人
Contact Person :

職位
Position :

樓面總面積
Total Floor Area : 2500 FT² (230 M²)

人手
Workforce : (i) 管理階層 Management 1

(ii) 生產部 Production 7

危險品貨倉的類別（如有者）
Category of D.G. Store : NO
(if any)

危險品貨倉的所在地（廠內／外）
Location of D.G. Store : NO
(within/outside factory)

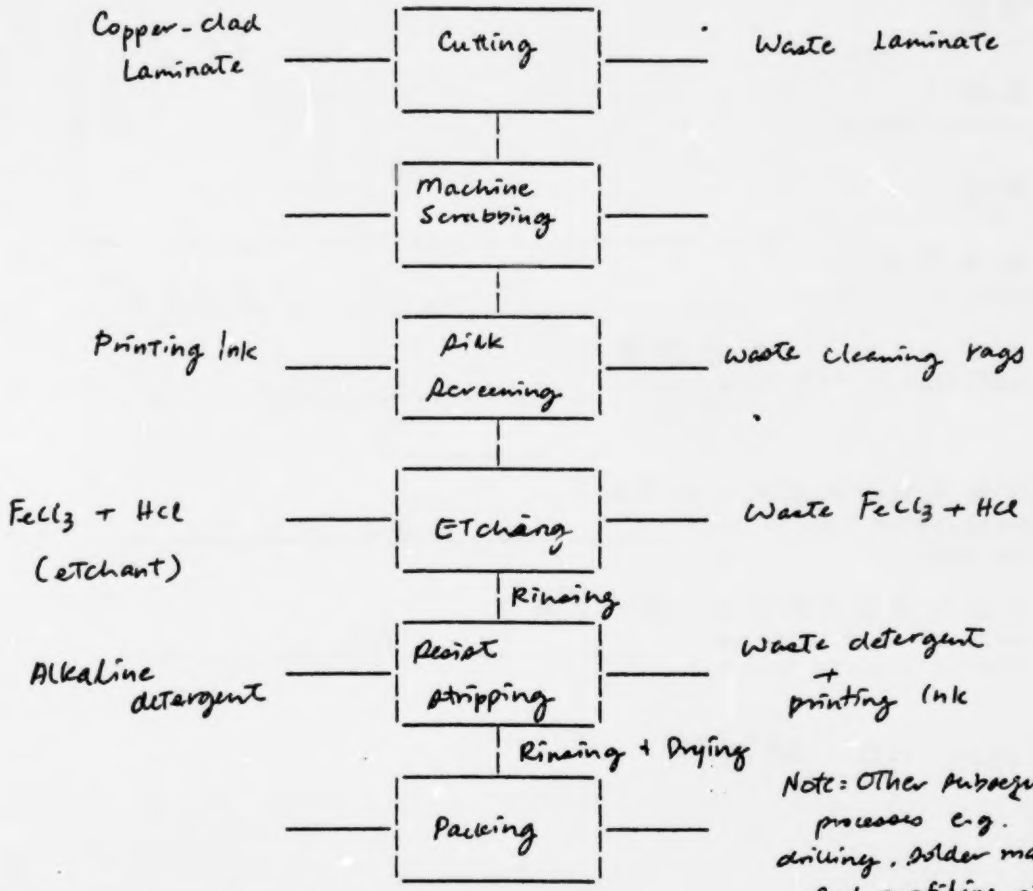
ISIC NO : 383435

生產詳情
.II. PRODUCTION DETAILS :

產品（種類及數量）
(a) Products (Type and Quantity) : Single - sided printed Circuit board

生產過程（請說明使用的化學品及廢料的產生過程）
(b) Production Processes : (please identify chemicals used and waste streams)

Material（生產之原料） **Process**（工序） **Waste**（產生之廢料）


Copper-clad Laminate
Cutting
Waste Laminate
Machine Scrubbing
Printing Ink
Silk Screening
waste cleaning rags
$FeCl_3$ + HCl (etchant)
Etching
Waste $FeCl_3$ + HCl
Rinsing
Alkaline detergent
Resist stripping
Waste detergent + printing ink
Rinsing + Drying
Packing

Note: Other subsequent processes e.g. drilling, solder masking and profiling etc. to be carried out in another factory in Shenzhan, China

未加工的原料（種類）
(c) Raw Materials (Types of materials) :-

II. (d) Chemical Consumption (所用化學品之種類):-

	Chemical 化學品	Average Consumption Rate/Month 每月平均用量	Dilution Factor 稀釋比例	貯存方法 * Method of Storage D.G. Store 危險倉	Lockers 貯物櫃	Anywhere Inside Factory 工廠內其他地方	包裝之方法 Package Form Materials & Size of Containers 容器之物料及尺寸
ACIDS 酸	HCl	520 L.	Use with $FeCl_3$			✓	25 L jerricans
ALKALIS 鹼	Alkaline detergent	235 kg	1:2			✓	25 kg Plastic Bags
METAL SALTS 金屬鹽							
CYANIDES 山埃							
SOLVENTS 溶劑							
PAINTS 油漆							
ADHESIVES 接合劑							
OILS 油劑							
DETERGENT 清潔劑							
DYES 染料							
PETROLEUM 汽油類							
FLAMMABLES 易燃物品類	Thinner	100 l/month				✓	25L jerricans
PRINTING INK 油墨	Printing Ink	2.5 kg				✓	5L./Tins
OTHERS 其他	$FeCl_3$	2600 kg	1:4			✓	50kg/Tins

(e) Water Consumption : 280 m³/month 每月之耗水量

* Please tick where appropriate

請於適當位置 ✓

III. WASTE INFORMATION :- 廢料之資料

(a) Liquid Effluent (Quantity and characteristics) :- 液體廢料（數量及特性）

Waste Stream 廢料來源	Quantity/ Frequency of arising 數量及排放次數	* Method of Disposal 處理方法 *					Remarks 備註
		Recycling 循環	Down the sewer 排水渠	Dispose with ordinary solid municipal waste 一般之市政垃圾	Sold to scrap dealers 賣給收集者	經處理後排放 Dispose after treatment (Please specify treatment method) （請詳述）	
Rinse water（洗水）	~ 280 m^3/month		✓				
（酸/鹼） Spent Acids/Alkalis							
Alkaline detergent	18 l/day		✓				
HCL	mixed with						
	$FeCl_3$						Disposed with $FeCl_3$ wastes (see below)
Plating Bath（電鍍缸）							
Spent Solvent （溶劑）							
Thinner	Some cleaning rags. (not much)						Most thinner used are volatilised during the process.
（潤滑油） Waste lubricating oil							
Waste cutting oil（切削油）							
Spent etchant（蝕刻物）							
$FeCl_3$	400 l/day		✓				Including waste HCl.
（其他） Any other process effluent							

* please tick where appropriate
請於適當位置 ✓

III. (Continued)

(b) Solid/Sludges (Quantity and characteristics) 固體／渣滓（數量及特性）

Waste Stream 廢料來源	Quantity/ Frequency of arising 數量／排放次數	* Method of Disposal 處理方法			Remarks 備註
		Dispose as ordinary solid waste 一般之市政垃圾	Sold to scrap dealers 賣給收集者	經處理後棄置 Dispose after treatment (Please specify treatment method) （請詳述）	
Plating bath sludge 工序之渣滓					
油缸之渣滓 Oil tank cleaning sludge					
Tannery waste 皮革廢料					
Printing waste 油墨廢料					
Dyestuff waste 染料廢料					
Paint waste 油漆廢料					
Toxic metal 有毒金屬廢料					
Metal oxides 金屬氧化物					
有機／無機廢料 Waste inorganic/organic solids					
Batteries 電池					
受污染之容器 Contaminated containers					
Any other process sludge 其他					

貴廠是否有廢料還原的設備？如果有，請詳述之：—

IV. Are there any facilities for waste recycling? If yes, please provide details :-

NO.

貴廠址之用地分配情況：—

V. Area usage within your factory :-

		百分率 Percentage %
Office 寫字樓		2 %
化學品之貯存 Storage area for chemicals		0.5 %
未完成工件，工具等之貯存 Storage area for unfinished products/tools/etc.		30 %
生産之用地 Production Area :-	(i) 預備／裝配 Preparation/assembling	17.5 %
	(ii) 生産過程之機械／儀器((i)項除外) Occupied by production machinery/equipment (excluding (i))	50 %

投資數據：—（此等資料是用作幫助本部門了解貴工業之情況，全部資料均會予以保密）

VI. Investment Figures :- (These data are used to assist us in understanding the profile of your industry, data will be kept confidential)

設置一間類似貴工廠規模所需之費用（估計）
(a) Estimated investment cost required for a similar new factory : $ 1,000,000

主要生產機械／儀器之一般壽命：
(b) Life span of major production equipment/machineries $ 7 yrs

操作費用（包括所有支出）
(c) Typical monthly operating cost :- (including all charges/expenses) $ 700,000 (including the cost in china)

操作費用之分類：—
(d) Breakdown of typical monthly operating cost :
(i) 工資 wages 84,000
(ii) 水費 water 600
(iii) 電費 electricity 15000 (including the electricity in chin.
(iv) 租金 rent 15,000 + (5000 in china)
(v) 原料 material 500,000 (including the material used in china)
(vi) 其他 others 80,400 (including exp. in china)

每月之營業額
(e) Typical monthly turnover $ 800,000.

Estimated profit = ~ 100,000 per month.

AEROBIC MINERALIZATION OF ORGANIC CONTAMINANTS BOUND ON SOIL FINES

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ABSTRACT

The goal of the overall research program, a part of which is discussed in this paper, is to demonstrate a sequence of aerobic/anaerobic microbial process steps for degradation of contaminated soil fines and slurries of soil fines. Toward this end, it must be possible i) to assay individual organic species and total contaminant organic carbon in soils of varying properties, ii) to separate whole soils into fractions according to particle size, and iii) to assay [as in i)] reactor slurries containing suspended soil particles, microbial culture and dissolved, dispersed and sorbed organic contaminants and metabolites. These techniques are required to define the nature of the contamination, devise operating conditions to facilitate microbial contact, and assure complete mineralization of target contaminations and "clean" residuals.

The first major section of this paper describes the development of analytical methodology for whole soil and soil fractions; in parallel, techniques for mixing/homogenizing, fractionation and extraction used in sample preparation are discussed. It has been possible to separate soil fines and some "bulk" organic matter. A large part of the total organic chemical contamination is due to sorption and physical pore interactions with the fine particle fractions [clay minerals and humic substances] of whole soil.

A second section describes microbial degradation experiments. Systems and procedures for microbial reactions were designed and implemented to accomodate the properties and behavior of target substrates. Both shake flask and fermentation reactions are being carried out on slurries of soil fines. Low molecular weight polynuclear and chlorinated aromatic hydrocarbons are readily biodegraded.

INTRODUCTION

Distillation bottoms and sludges from benzene-toluene-xylenes [BTX] production were impounded for several decades. The production process consisted of the catalytic cracking of naphtha, in the presence of fuming sulfuric acid, and distillation. Therefore, lagoon contents include naphtha-related compounds, distillate residues and compounds resulting from reactions of these species and sulfuric acid. Possible contaminants include, but are not limited to, simple aromatic species, polynuclear aromatic hydrocarbons [PAHs], phthalates, as well as sulfonated derivatives of these compounds. Many of these species have slight solubility in water and/or an affinity for some of the constituents of soil and have migrated into and through the soil immediately adjacent to the lagoon.

During this study, soil samples were obtained from the containment area surrounding the lagoon. The impoundment has been designated a CERCLA-NPL site; it exceeds ten acres in extent and contains an estimated 100,000 cubic yards of residues. The contents of the lagoon have separated into several distinct layers that include, in bottom-to-top sequence, a solid mixture of organic and inorganic substances, a tar-like layer, a layer of viscous organic matter, and a floating aqueous layer.

ANALYTICAL APPROACH

Initially, soil samples are mixed and homogenized. The resulting material is air-dried and sieved through a 3-cm brass screen to remove debris, rocks and gravel; this procedure also breaks up macro-agglomerates. A second sieving, with a 5-mm screen, improves homogeneity, enhances mixing and helps toward analytical reproducability. Direct solvent extractions of homogenized, contaminated soil utilize methanol, cyclohexane, or methylene chloride. Methanol has relatively high polarity, cyclohexane is a model cyclic compound, and methylene chloride is a moderately polar, volatile compound with broad solvent capabilities.

Gas chromatography [GC] is used to identify and quantify compounds in soil extracts. USEPA Test Methods 602 and 610 are employed in these analyses. Method 602 is used to assay aromatic species in GC column effluent with a photoionization detector [PID] in series with an electrolytic conductivity detector [ELCD]. Method 610 is employed to detect PAHs and phthalates, utilizing a flame ionization detector [FID]. Standard solutions are assayed in sequence with solvent solutions to match retention times for compound identifications. Peak areas are used to construct standard curves and provide a basis for determination of contaminant concentrations. Compound concentrations are calculated from both PID and FID output to check analytical consistancy.

Experimental Methods

Soil contaminant levels were initially estimated to fall between 2 and 5 % on a dry weight basis. Direct solvent extractions are carried on varying masses of soil with the goal of limiting contaminant concentrations to about 100 mg/L in extract solutions. This target concentration was adopted to avoid overloading the detectors. Soil masses varying from 0.15 to 0.38 g are extracted with a fixed volume of solvent.

Duplicate amber serum bottles, each

with label, septum and aluminum cap, are weighed with a Mettler PE3600 balance. Bottles are 100 mL in volume. Soil is added until target weights are attained; approximately 50 mL of methanol, cyclohexane or methylene chloride is added to both bottles. Bottles are sealed with the septa [Teflon-coated neoprene] and reweighed. Experimental errors include the small discrepancies in obtaining target soil masses and measuring solvent volumes. In general, these are accounted for in concentration calculations. A second form of the experiment is carried out to facilitate compound identification. It is the same in all respects, except that 20 g of soil are added; since quantification is not desired, duplicates are not performed.

Extraction vessels are shaken for approximately one hour. This time was found to be adequate in earlier studies; however, it assumes that only readily reversible, high-rate sorption processes are involved. Higher energy binding processes and sorbate trapped by capillary forces would not participate in such short-term partitioning. Extract solutions are filtered through 0.2-um MSI Cameo II 25-mm disposable syringe filters, into duplicate 5-mL vials. Samples are stored at 4°C, to minimize volatilization losses, and enclosed to exclude light and avoid photolytic chemical reactions.

Method 602 utilizes a 1.8-m long by 2-mm ID stainless steel GC column packed with 100/200 mesh Supelcoport, coated with 5 % SP-1200 and 1.75 % Bentonite-34. Oven temperature is held at 50°C for 2 min; a 6°C ramp takes the oven to 90° for a final period of 23 min. The PID has detection limits of 1 to 10 pg for unsaturated carbon bonds found in aromatic compounds. The ELCD has detection limits of 0.1 to 1 pg when used in the detection of chlorinated compounds or to verify PID results. Sample size is 2 uL. Method 610 is applicable to PAHs and phthalates. It utilizes a 1.8-m long by 2-mm ID glass GC column packed with 100/200 mesh Chromosorb W-AW-DCMS, coated with 3 % OV-17. Oven temperature is held at 100°C for 4 min; a 8°C ramp takes the oven to a final temperature of 280°C. The FID has detection limits of 10 to 100 pg. Sample size is 5 uL.

Chemical Oxygen Demand [COD] is determined for some contaminated soil samples. This procedure is identical to that described in Standard Methods". The COD has some value for comparison with carbon in identified species, to estimate extraction and identification efficiencies.

Analytical Results

Extracts generated in Experiment 12888 were distinctly different in color. After filtration, the cyclohexane extract was translucent orange, methylene chloride gave an opaque brown liquid, and the methanol solution was clear and tan. This appeared to be evidence for susbtantial variation in extraction efficiency. In addition, the high polarity of methanol leads to destruction of soil aggregates; thus, methanol is capable of extracting contaminants held in micro- and macro-pores by capillarity and interfacial tension. Solvents can be compared on the basis of the mass of naphthalene extracted. No naphthalene was extracted by cyclohexane; methanol and methylene chloride extracted 1,089 and 1,403 mg/kg dry soil, respectively. Thus, for naphthalene, solvent power varied considerably.

The PID sees cyclohexane and

impurities in methylene chloride. The ELCD detects chlorinated compounds and is overloaded by methylene chloride solutions. The consequence is chromatogram baseline fluctuations and large peak area integration inaccuracies. Methanol was the only solvent suited to Method 602. Methylene chloride was used in conjunction with Method 610. Eight major organic compounds were identified and quantified in methanol solution. In order of decreasing concentration [mg/kg], they are: naphthalene - 1,090; 1,2-dichlorobenzene - 360; toluene - 150; xylene isomers - 145; benzene - 113; and, ethylbenzene - 28. The eight species account for 64 % of the total peak area of chromatographic responses.

Benzene, toluene and the xylenes are primary products of naphtha distillation. GC residence times for standard solutions and extract solutions, with PID detection, varied less than 0.004 sec for this group. Naphthalene is also a major component of naphtha; residence times differed by 0.004 sec. Ethylbenzene [EB] is formed by catalytic reaction of benzene with ethylene, an olefin found in industrial naphtha. In BTX production, sulfuric acid is the catalyst. EB residence times varied by 0.008 sec.

The appearance of 1,2-dichlorobenzene was signaled by the PID and verified by the ELCD, a halogen-specific detector. Chlorinated compounds are not normally found in naphtha nor are they produced by sulfuric acid catalysis. The presence of this compound may indicate disposal to the impoundment from another manufacturing source or a spill clean-up activity. Two substantial, unidentifiable peaks were encountered with Method 610; neither was observed with Method 602. These peaks correspond to compounds that are believed to be sulfonated aromatic hydrocarbons; operating temperatures for Method 602 preclude elution of such higher boiling species. Naphthalene sulfonic acids represent compounds of higher molecular weight and boiling point, requiring increased GC oven temperatures [Method 610] and extended residence times.

Standard solutions included seven purgable aromatic compounds in methanol [see Table 1a] and fifteen PAHs in a 50:50 methanol:methylene chloride mixed solvent [see Table 1b]. Gas chromatograms are obtained by Method 610 for the PAH standard solution and methanol extract, respectively. Similarly, are GC outputs are obtained by Method 602 for the purgable aromatic standard and the methanol extract, respectively. Naphthalene is run with a modified version of Method 602.

COD has been measured for several soil samples. This assay is used to determine the total oxygen required to fully oxidize all reduced species; it does not distinguish between contaminant organic carbon and hydrogen, soil organic matter, and metals in reduced or partially oxidized states. The COD of sieved, air-dried, unextracted soil corresponds to about 50 mg C/kg soil. In comparison, the total organic carbon [TOC] associated with the eight quantified contaminant species cited above is approximately 1.6 mg C/kg soil or 3.2 % of the COD carbon equivalent. This is not a reflection of extraction efficiency. However, CODs run on soil samples taken at points remote to the disposal lagoon average close to 50 mg C/kg soil. Thus, extraction efficiency with methanol is probably relatively good.

Table 1a

Purgable Aromatic Standard Mixture [602-M] (in Methanol)

Compound	Concentration (mg/L)
Benzene	2000
Toluene	2000
Ethylbenzene	2000
Chlorobenzene	2000
1,2-Dichlorobenzene	2000
1,3-Dichlorobenzene	2000
1,4-Dichlorobenzene	2000

Table 1b

Polynuclear Aromatic Hydrocarbon Standard Mixture [610-M] (in 50:50 Methanol:Methylene Chloride)

Compound	Concentration (mg/L)
Acenaphthene	1000
Fluoranthene	200
Naphthalene	1000
Benzo(a)anthracene	100
Benzo(a)pyrene	100
Benzo(b)fluoranthene	200
Benzo(k)fluoranthene	100
Chrysene (93 %)	100
Acenaphthylene	2000
Anthracene	100
Benzo(g,h,i)pyrene	200
Fluorene	200
Phenanthrene	100
Dibenzo(a,h)anthracene	200
Indeno(1,2,3-cd)pyrene	100
Pyrene	100

MICROBIAL APPROACH

The solubilities of PAHs in aqueous media decreases with increasing molecular weight; for four rings or more, saturation concentrations are very low and difficult to measure. Within this context, rates of aerobic metabolism of PAHs are insignificant. In addition, this class of aromatic compounds has a high affinity for several constituents of natural soils, i.e., soil organic matter [humic substances] and clay minerals. PAHs are lipophilic, i.e., prefer sorptive association and/or dissolution in organic rather than hydrophilic phases. In addition, many multi-ring molecules can migrate into stable positions inside clay mineral structures, either diffusing between laminae in mica-like structures or entering the crystal lattice directly. The latter process is a form of clathration. These preferred soil components are, in general, the smaller particle fractions of the soil system. Thus, it is possible to introduce PAHs into a microbial systems in slurry form, with substrate(s) bound to particulate matter.

A slurry form of bioreactor has a number of possible thermodynamic phases present, including: aqueous medium with dissolved substrate and nutrients, substrate bound to soil particles, suspended single and clustered cells, substrate emulsions and colloids, and cells attached to the exterior and macro-pore surfaces of dispersed particles. Sampling and analytical methodology are difficult throughout the design and implementation of biodegradation experiments.

An earlier Section dealt with the problems of accurate chemical contaminant identification and quantification for soils prior to chemical or biochemical reaction. Often tightly-bound PAHs must be extracted from a soil mass, with uncertain efficiency or recovery. Method verification is critical. Extract solution is assayed by GC or High Performance Liquid Chromatography [HPLC]. Multiple phases must be sampled and extracted, during and after biochemical transformations. The possible appearance of intermediate or final metabolites, i.e., incomplete mineralization, adds to the complexity of mass balances for substrate species. COD is a useful tool for quasi-continuous monitoring of the progress of slurry-type bioreactor systems. In well-aerated aqueous systems, metals are not a serious factor. However, variable cell mass and natural soil organic matter severely limit this approach.

Before slurry reaction can be undertaken, whole soil must be reduced to several particle size fractions. Contaminant PAHs favor finer particles, thus, fractionation is a useful way of concentrating these compounds prior to degradation experiments. A reproducible method for soil classification has been developed and has been demonstrated to lead to the desired concentration of target substrates, as follows. Whole soil is separated into three phases: a tar-like organic phase, a coarse sandy phase and an aqueous suspension of soil fines. The latter is suited to slurry reactor experiments. Experiments consist of small-scale studies in shake flasks, performed in matrix formats, and fermentation studies in reaction vessels of larger volume.

Background

The rates of microbial assimilation of PAHs have been demonstrated to be functions of solubility, molecular weight, number of six-member rings, degree and type of substitution, as well as environmental conditions, such as temperature, pH and oxygen concentration. The solubility of unsubstituted PAHs,in water, drops sharply as the number of rings increases. It rapidly diminishes to levels that are too low to support significant biological activity; see Table 2 for data. Compounds of six or more rings have vanishing solubility in water.

The number and type of substituents on or in a PAH molecule have a marked influence on solubility. The solubilities of phenols, nitrogen heterocyclics, polynuclear polyols, sulfonates and other mono- and poly-substituted PAHs are often significantly higher than the basic hydrocarbons. Therefore, substituted compounds are more likely to be observed as solutes in contaminated groundwater. Also, surfactants increase PAH solubility. However, these compounds complex or "react" with the high molecular weight polynuclear species to create a composite hydrophilic exterior. The result is either a stable emulsion, colloidal suspension or micro-dispersion; it cannot properly be classed as dissolution in the thermodynamic sense of a homogeneous liquid phase. Sodium laurylsulfate increases the solubility of 2- to 7-ring PAHs by 2 orders-of-magnitude or more.

Biodegradation of 2- to 3-ring PAHs by pure microbial cultures has been demonstrated; naphthalene, phenanthrene and anthracene have been shown to be assimilated quantitatively. Higher molecular weight compounds, i.e., benzo(a)anthracene and benzo(a)pyrene, can be degraded to simpler intermediates in the presence of supplementary carbon sources or cometabolites, i.e., biphenyl and succinate.

Bacteria concentrate, grow, and form bioslimes in aqueous boundary layers at liquid/liquid and liquid/solid interfaces. Organic cosolvents can transport PAHs to such interfaces and increase the rate of biodegradation. There is no information to support microbial metabolism of solid PAHs; similarly, there is little data on the bioreaction of PAHs sorbed on nonreacting surfaces.

Experimental

i) Apparatus

Aerobic biodegradation experiments are carried out in 60-mL Ehrlenmeyer flasks, on a laboratory shake device, or in 3-L [working volume] fermentation vessels. The shaker studies are arranged in matrix format with the following common composition: 30 mL soil slurry, 20 mL inoculum and 10 mL nutrient medium [see Table 3]. The composition of the inoculum is varied to provide a basis for the evaluation of substrate volatility losses, reactor surface wetting and sorption onto biomass as mechanisms of substrate disappearance. The 20 mL "inoculum" is live culture; in sterile controls, the 20 mL of seed is replaced by autoclaved culture or deionized water. Controls are intended to illustrate the extent to which volatilization and inorganic surface sorption influence substrate fate. Given that biomass rendered unviable by autoclaving retains substantial sorption capacity, autoclaved culture is designed to investigate this loss pathway. Also, this control provides a zero-time or baseline measurement for carbon or oxygen demand. The pH of the composite solution is adjusted to 7.15 by addition of a mixture of solid potassium monobasic and dibasic phosphates.

Fermentation studies are carried out with a working volume of 3 L prepared in the same ratio of 3:2:1 for soil slurry:inoculum:nutrient medium as in the shake flask studies. The reactor is sparged with air at the rate of 5 to 6 L/min; it is stirred at 300 rpm. The pH is maintained at 7.15 by periodic additions of 0.25M sodium hydroxide regulated by a pH controller. Samples are taken at 24-hr intervals, to monitor the course of reaction. Separate studies utilizing deionized water are used to evaluate volatilization losses.

ii) Soil Slurry

Soil slurry is prepared by a sequence of homogenization, extraction, and fractionation steps. This procedure is designed to create a suspension of soil fines that displays minimum variation from batch-to-batch. Whole soil samples are homogenized by passing the air-dried material through a 5-mm screen, quartering the resulting solids cone through the apex, segregating the quarters, and sieving each quarter to form a new cone. Soil is sieved three times. A prescreening with a 3-cm sieve removes rocks and miscellaneous debris and, also, serves to break-up larger clumps of packed soil.

Homogenized soil [84 g on a dry basis] is extracted with 350 mL of water at pH 7. Extraction separates the contaminated soil into three phases: a tar-like [smell, sticky, viscous, etc.] organic phase corresponding to 0.65 - 0.75 % of the initial dry mass; a mixture of larger, heavier particles [sand]; and, an aqueous supension [slurry] of fine soil particles. The aqueous suspension is separated from the settleable solids by screening through a 10-micron sieve; filtered solids are washed with 650 mL of water to dilute the filtrate slurry to 1 liter and the final concentration. The fractionation procedure has been found to retain approximately 65 % of the initial dry mass of soil on the sieve. The final slurry of fine particles is stable and does not show any evidence of settling under experimental conditions.

iii) Inoculum

The aerobic inoculum is obtained as waste sludge from the Somerset/Raritan Valley Sewage Authority.

iv) Nutrient Medium

The nutrient medium is prepared from a conventional recipe for aerobic cultures and does not employ a primary or supplementary carbon source; see Table 3. The soil slurry supports microbial activity without the use of a co-substrate; none is added.

v) Analytical

The progress of substrate conversion is monitored by COD and GC analyses. Samples are prepared for the latter by extraction with methylene chloride at 8 mL of solvent for 20 mL of slurry. The remainder of the assay is carried out in accordance with USEPA Method 610. A 1.8-m long by 2-mm ID glass column is packed with a stationary phase consisting of 100/200 mesh Chromosorb W-AW-DCMS coated with 3 % OV-17. Oven temperature is held at 100^oC for 4 min; a 8^oC/min ramp increases the temperature to 280^oC. An FID is used to determine residence times and peak areas. Gas pressures are 70, 40 and 65 psi for nitrogen, hydrogen and dry air, respectively. A 5-uL sample is injected into the GC.

Results

Table 4 summarizes moisture contents and COD analyses for whole soil and the fractions generated by repeated sieving, fractionation and extraction. COD determinations are referred to 1 kg of air-dried whole soil. The COD balances vary about 15 % for a typical set; this is a consequence of an error of at least ± 5 % in this measurement. Slurry, diluted with wash water, has a COD of 7.1 g O_2/L.

When an active microbial inoculum is combined with a slurry of soil fines, a lag period of approximately 6 hr is observed. Acid production in shake flasks and fermentations, and carbon dioxide generation by fermentations, are not observed until after the lag phase. There is no loss of COD, as might accompany volatilization or sorption. It is assumed that COD attributable to biomass remains unchanged during the experiment, i.e., growth is negligible. The reduction of COD in the flasks inoculated with live cultures is indirect evidence for substrate mineralization, as opposed to physical uptake (sorption) by the biomass. The results of a shake flask matrix study are summarized in Table 5. Flasks contain a working volume of 60 mL; total reaction time is 80 hr. The slurry has an initial soil fines concentration of 30 g/L and a COD of 7.0 g O_2/L; inoculum COD is 4.75 g O_2/L.

Table 6 sumarizes results of a larger scale fermentation study. Reactor working volume is 3 L and reaction time is 68 hr. The slurry has an initial soil fines concentration of 45 g/L and a COD of 7.5 g O_2/L; as in the shake flask illustration, inoculum COD is 4.75 g O_2/L. Initial reactor COD was calculated to be 15.9 g O_2; an experimental determination gave 18.9 g O_2. The difference is probably measurement error, due to the several phases present, i.e., cells, contaminated fines, suspended tarry material and dissolved PAHs. A volatilization loss study was carried out with the fermentor. The COD of air sparged slurry did not change in 4 days; it remained at 3.1 g O_2/L.

Figures 1 and 2 are gas chromatographs for the fermentation liquor after 21 hrs and at the end of the experiment. The characteristics of the soil slurry without medium or culture added are described in Figure 3. The contents of the fermentor and the original soil slurry were extracted with methylene chloride; the volume ratio was 5:2 for aqueous suspension:solvent. Figures 1 and 2 show definite declines in the number and size of peaks, especially those corresponding to low molecular weight PAHs.

CONCLUSIONS

1) Bench-scale shake flask studies are performed with slurries of soil fines and mixed microbial seed. COD, corrected for the presence of the inoculum growing at a trivial rate, is reduced by 50 % in approximately 80 hours. Similarly, TOC is measured on settled [filtered] aqueous phase and remains low throughout. The latter assays are a reflection of limited hydrocarbon solubilities.

2) Larger-scale fermentations are carried out in 3-liter, stirred, air-sparged reactors. Inoculum and nutrient medium are mixed with slurry. Biodegradation is monitored by assays on samples of aqueous

dispersions and measurement of carbon dioxide generation rates. COD reductions exceed 84 % in 68 hours.

3) Whole soil is separated into size fractions to characterize contaminant distribution by soil constituent type and particle size. It is possible to separate whole soil into larger, settleable particles [primarily sand and silt], slurried fines, a clarifiable aqueous phase and a bulk organic phase. Recovery of initial whole soil COD in the slurry and a tar-like organic phase is nearly quantitative.

4) Analytical techniques have been developed and demonstrated with whole soil, soil fractions, slurries of fines and filtered liquids. These techniques are essential to the identification of contaminant species and quantification of individual and total contaminant concentrations. Assays are necessary to define initial and intermediate conditions and to demonstrate that contaminant destruction [mineralization] by microbial reaction is effective and approaches completeness.

Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

Table 2. Solubilities of PAHs in Water

Compound	Mol. Wt.	Solubility (ug/L)	# of Rings
Naphthalene	128	31,700	2
Acenaphthene	154	3,200	3
Fluorene	166	2,000	3
Phenanthrene	178	1,300	3
Anthracene	178	73	3
Fluoranthene	202	260	4
Pyrene	202	140	4
Benzo(a)pyrene	252	4	5
Dibenzanthracene	278	>1	5

Table 3 - Medium Composition

Constituent	Concentration [mg/L]
$(NH_4)_2SO_4$	1,500
$MgSO_4.7H_2O$	100
$FeCl_3.6H_2O$	0.5
$MnSO_4.H_2O$	10
$CaCl_2$	7.5

Table 4 - Moisture Content and COD

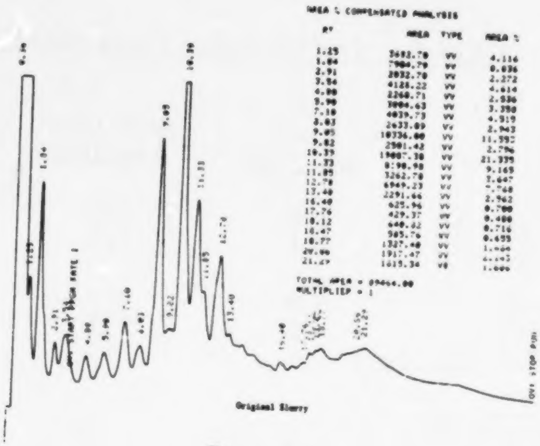
Sample Type	Composition [%]	COD [g O_2/kg]
Whole Soil	--	89.6
Water	16	0
Large Particles	53	trace
Soil Fines	31	--
Tar-like Residue	--	19.4
Slurry	--	84.5

Table 5 - Typical Shake Flask Matrix Study

	Live Inoculum	Autoclaved Inoculum	No Inoculum
Initial COD [mg O_2]	310	310	210
Final COD [mg O_2]	204	318	240
COD Change [%]	-34	nil	+14
COD Change [%] (corrected for inoculum)	-50	nil	+14
Final Dissolved TOC			
[mg C]	8	8	8
[mg C/L]	131	131	133
COD Equivalent [mg O_2]	18	18	18

Table 6 - Fermentation Study

	21 hrs	46 hrs	68 hrs
COD [mg O_2]	13200	10200	6900
COD Change [%]	30	46	63
COD Change [%] (corrected for inoculum)	39	61	84
Final Dissolved TOC			
[mg C]	318	315	288
[mg C/L]	106	105	96
COD Equivalent [mg O_2]	848	840	768



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AREA % COMPENSATED ANALYSIS

  RT              AREA   TYPE     AREA %

  1.25          3682.70   VV       4.116
  1.84          7994.79   VV       8.936
  2.91          2032.70   VV       2.272
  3.54          4128.22   VV       4.614
  4.88          2268.71   VV       2.536
  5.90          3004.63   VV       3.358
  7.10          4039.73   VV       4.515
  8.03          2633.09   VV       2.943
  9.05         10336.00   VV      11.553
  9.82          2501.42   VV       2.796
 10.39         19087.38   VV      21.335
 11.33          8198.98   VV       9.165
 11.85          3262.70   VV       3.647
 12.78          6949.23   VV       7.768
 13.40          2291.66   VV       2.562
 16.40           625.96   VV       0.700
 17.76           429.37   VV       0.480
 18.12           640.62   VV       0.716
 18.47           585.76   VV       0.655
 18.77          1327.40   VV       1.484
 20.06          1917.47   VV       2.143
 21.29          1619.34   VB       1.810

TOTAL AREA = 89464.00
MULTIPLIER = 1
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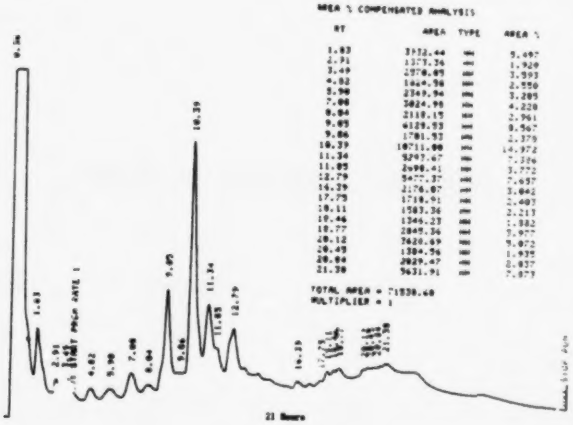
Figure 1



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AREA % COMPENSATED ANALYSIS

  RT              AREA   TYPE     AREA %

  1.83          3932.44            5.497
  2.91          1373.36            1.920
  3.49          2570.05            3.593
  4.82          1824.98            2.550
  5.90          2349.94            3.285
  7.08          3024.98            4.229
  8.04          2118.15            2.961
  9.05          6129.53            8.569
  9.86          1701.53            2.379
 10.39         10711.00           14.974
 11.34          5297.67            7.406
 11.85          2698.41            3.772
 12.79          5477.37            7.657
 14.39          2176.07            3.042
 17.79          1718.91            2.403
 18.11          1583.36            2.213
 18.46          1346.23            1.882
 18.77          2845.36            3.977
 20.12          3620.69            5.062
 20.49          1384.96            1.936
 20.84          2029.47            2.837
 21.30          5631.91            7.873

TOTAL AREA = 71530.60
MULTIPLIER = 1
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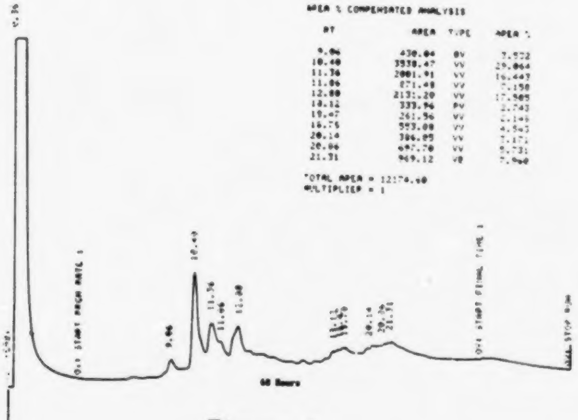
Figure 2



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AREA % COMPENSATED ANALYSIS

  RT              AREA   TYPE     AREA %

  9.96           430.04   BV       3.532
 10.40          3538.47   VV      29.064
 11.36          2001.91   VV      16.443
 11.86           871.48   VV       7.158
 12.80          2131.20   VV      17.505
 18.12           333.96   PV       2.743
 19.47           261.56   VV       2.148
 19.75           553.08   VV       4.543
 20.14           386.05   VV       3.171
 20.86           697.70   VV       5.731
 21.31           969.12   VB       7.960

TOTAL AREA = 12174.40
MULTIPLIER = 1
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Figure 3

ENVIRONMENTAL FATE MECHANISMS INFLUENCING BIOLOGICAL DEGRADATION OF COAL-TAR DERIVED POLYNUCLEAR AROMATIC HYDROCARBONS IN SOIL SYSTEMS

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ABSTRACT

Biodegradation is a technically viable and cost effective approach for the reduction and immobilization of polynuclear aromatic hydrocarbons (PAH) present in contaminated soils and sludges associated with coal-tar derived processes. While it is widely reported and accepted that PAH biodegradation in soil systems does occur, the specific controlling mechanisms are not entirely understood. One common observation among published reports is that the more soluble, lower molecular weight PAH compounds are biodegraded to a greater extent than the less soluble, higher molecular weight PAHs.

The rate and extent to which PAHs are removed from soil/sludges is influenced by the combined and simultaneously occurring effects of volatilization, sorption and biological oxidation. The degree to which each of these three environmental fate mechanisms occurs is mainly influenced by the physical/chemical characteristics of the contaminated media, the physical/chemical characteristics of the specific PAH compounds, and the design and operation of the particular biological treatment process.

Past researchers have interpreted reductions in PAH soil concentrations via biological treatment using first-order biodegradation kinetic rates. Recent work by the co-authors indicates that sorption and biological oxidation are interconnected phenomena and that PAH reductions are attributable to a combination of these effects. For PAH compounds to be susceptible to biological oxidation, it is postulated that they must be available to the bacteria by diffusing into the bulk aqueous liquid present in the macropores of the soil matrix. If this desorption/diffusion does not occur, then it follows that biodegradation may be impeded.

Under this scenario, PAH desorption from the solid material and subsequent aqueous phase diffusion may be the rate- limiting steps and, hence, control the rate and extent of both volatilization and biological oxidation.

INTRODUCTION

The viability of biological treatment processes rests on the ability to degrade and immobilize soil contaminant concentrations to acceptable levels through biological and chemical transformations. At the same time, volatile emissions and leachate from the treatment unit must be controlled below levels that would cause public health or environmental concern. Using the results of laboratory and field experiments, in conjunction with transport and fate analysis of soil contaminants, a biological treatment process can be designed and operated to: (i) maximize residue degradation and immobilization, (ii) minimize release of dust and volatile compounds, (iii) minimize percolation of water soluble compounds, and (iv) control surface water run-on and runoff. The applied material can be liquid, semi-solid, or solid. Detailed discussions of relevant processes are given elsewhere [1, 2, 3, 4,5, 6, 7].

Polynuclear aromatic hydrocarbons (PAH) are neutral, non-polar organic compounds consisting of two or more fused benzene rings in linear, angular, or cluster arrangements. Due to the acute and chronic toxicity primarily associated with the lower molecular weight PAHs, and the potential carcinogenicity associated with the higher molecular weight PAHs, the United States Environmental Protection Agency (U.S. EPA) has designated sixteen PAHs as being environmentally important and representative of PAHs as a class of compounds. The sixteen are cited in Table 1 where they have been grouped on the basis of the number of aromatic rings comprising a particular compound. These are the same PAH compounds which are included in EPA's Priority Pollutant List [8]. While many other PAH isomers exist, this EPA list will be given focused attention in this paper.

Due to their toxicity at specific concentrations and the potential carcinogenicity of some higher ring PAHs, remediation of contaminated soils and sludges to achieve PAH reductions is often required. To this end, biological treatment has been widely researched and utilized to treat soils and sludges containing PAHs. Soils and sludges contaminated with coal-tar derived PAHs are associated with the industrial processes of creosote preservative wood treatment, coal tar distillation, coke manufacturing and manufactured gas plants. While it is widely reported and accepted that biodegradation of PAHs does occur, individual PAH compounds and isomers vary widely in their susceptibility to biodegradation with the specific controlling mechanisms not entirely understood [5, 6, 7, 9, 10]. One commonly cited observation indicates that the more soluble, lower molecule weight PAH compounds are generally biodegraded at a faster rate and to greater extent than the less soluble, higher molecular weight PAHs. This paper presents information which begins to elucidate the fate mechanisms which appear to influence the rate and extent of PAH reductions achieved through biological processes. Focus is given to both applicable theory and results of laboratory and field biological treatment applications. While PAHs are specifically addressed, the concepts presented may also be applicable to other organic compounds, e.g. volatile aromatics, pentachlorophenol and PCBs.

TWO RING	***THREE RING***	***FOUR RING***	***FIVE RING***	***SIX RING***
Naphthalene	Acenaphthene	*Benzo(a)anthracene	*Benzo(b)fluoranthene	*Benzo(g,h,i)perylene
	Acenaphthylene	*Chrysene	*Benzo(k)fluoranthene	*Indeno(1,2,3cd)pyrene
	Anthracene	Fluoranthene	*Benzo(a)pyrene	
	Fluorene	*Pyrene	*Dibenzo(a,h)anthracene	
	Phenanthrene			

NOTE: *Indicates potentially carcinogenic compound by EPA (11)

TABLE 1. POLYNUCLEAR AROMATIC HYDROCARBONS ON EPA'S PRIORITY POLLUTANT LIST

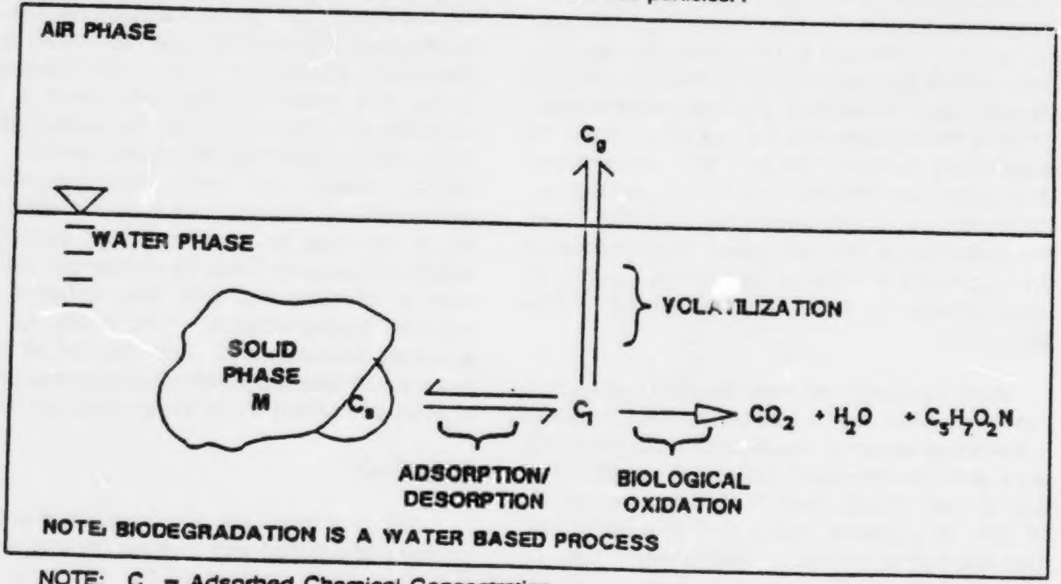
PURPOSE

The use of biological treatment processes for the remediation of PAH contaminated soil/sludges must be based on sound scientific and engineering principals. These principals must be thoroughly understood and manipulated to achieve final clean-up concentrations within specified time periods. This understanding also serves to justify clean-up concentrations on the basis of risk assessment considerations.

Environmental Fate Mechanisms

Based on a review of available literature, Sims and Overcash [5] and the U.S. EPA [8] cite volatilization, sorption, and biological oxidation as the three primary environmental fate mechanisms influencing PAHs in the environment. While photolysis, chemical oxidation, and bioaccumulation of PAHs may occur, they are not considered to be significant relative to the other three. Sorption refers to the combined and simultaneously occurring processes of adsorption/desorption and diffusion within the soil matrix.

On this basis, Figure 1 schematically illustrates the manner by which PAH removal from soils is most likely influenced by the combined and simultaneously occurring effects of volatilization, sorption, and biological oxidation during biological treatment in a soil-water system. Of these, the latter two fate mechanisms are cited as generally being the more predominant. These three fate mechanisms are in turn influenced by the physical/chemical characteristics of the particular PAH compound, the physical/chemical characteristics of the particular media, (e.g., soil, sludge, water), and the particular biological treatment system design and operation. The overall process depicted in Figure 1 models PAH biodegradation as a water-based process influenced by chemical partitioning among the solid, air, and water phases. In this model, biological oxidation can occur only if a particular PAH compound within or on a soil particle (C_s) desorbs and diffuses into the bulk water phase (C_l). Once in solution, volatilization (C_g) can also occur. While some volatilization of only the lower molecular weight, 2- and 3-ring PAHs may occur, it is not considered a major fate mechanism in most biological treatment processes [12]. In many instances, PAH desorption and diffusion into the bulk water phase may be the rate-limiting steps controlling both volatilization and biological oxidation; desorption and diffusion are generally considered separate processes. This model is supported by Annokkee [13] who cites that "the biodegradation reaction is rate limited primarily by diffusion of the organic material to the surface of the soil particles.".



NOTE: C_s = Adsorbed Chemical Concentration,
C_g = Gas Phase Chemical Concentration,
C_l = Liquid Phase Chemical Concentration

Figure 1. Role of Desorption/Diffusion in PAH Biodegradation

With specific reference to sorption processes, Figure 1 conceptualizes a soil matrix as a collection of porous, water-stable aggregates which are loosely associated with one another. Only a single soil aggregate is illustrated in Figure 1. The aggregates consist of organic and inorganic (e.g., clay) fractions which are ionicly bound together by metal cations such as aluminum. The size of the individual aggregates range from less than 1 to 250 microns in diameter. Soil water can exist in the macropores between the aggregates (bulk soil water) or within the micropores of the individual aggregates themselves (pore water).

It is believed that the micropores of the individual aggregates are large enough to permit some chemicals to move into, out of, and within the aggregate, but they are not sufficiently large to permit microorganisms to enter. Hence, for biodegradation to occur, the chemicals must migrate to the bacteria which exist at the surface of the aggregate or in the bulk soil water (macropores). The organic contaminant can be present in the soil system bound to the soil organic/inorganic fractions, in aqueous solution (either in the micropore water or the bulk soil water), or as a free hydrocarbon phase. As such, migration to the bacteria requires some combination of the adsorption/desorption, dissolution, and diffusion processes. Desorption and dissolution are the mechanisms by which the contaminant enters the solution and diffusion is the mechanism which governs its movement in the aqueous phase. It is generally believed that for PAHs, adsorption/-desorption and diffusion are critical parameters. Dissolution is not considered as important since the presence of the free phase hydrocarbon in the aggregate is unlikely due to the inability of hydrocarbons to enter the micropores of the aggregate.

Much research on PAH sorption processes has been done, and continues to be performed in soil/water systems. General conclusions of this work are that the lower molecular weight PAHs (i.e., 2- and 3-ring) have a tendency to desorb off soils to a greater extent and at a faster rate than the higher molecular weight PAHs (i.e., 4-, 5- and 6-ring). Due to their inherent physical/chemical properties, the concentrations of lower molecular weight PAHs in aqueous solution can be on the order of the part per million (ppm) range while the higher molecular weight PAHs are typically in the range of part per billion (ppb) to part per trillion (ppt). These differences in solubilities result in more extensive and faster rates of biodegradation for the lower molecular weight PAHs.

In the past, some researchers have attributed these differences in rates to the higher molecular weight PAHs being more recalcitrant to biodegradation than the lower weight PAHs. However, research work presented in this paper begins to support the premise that the lower biodegradation rates observed for higher molecular weight PAHs may be due more to their lack of bioavailability in solution at ppm concentrations. Specific discussions related to the three environmental fate mechanisms of sorption, biological oxidation and volatilization of PAHs in soil-water systems are given elsewhere [5, 8, 12, 14-17].

The significance of the hypothesis presented is amplified by the fact that soil aggregates which may have been in contact with contaminants for 50 years or longer will contain PAHs which may have penetrated deep into individual aggregates. An equally long period of time may be required for the same PAH compounds to desorb and to become available to biological oxidation treatment. Thus, treatment processes which rely on the availability of the contaminant in the bulk liquid phase will most likely be rate-limited by this desorption/diffusion process. This conceptual model may help to explain why there is such variability reported with regard to biodegradation rates and achievable treatment levels. This model relates to soil desorption/diffusion processes in an aqueous environment without the aid of chemical amendments (e.g., surfactants) which may serve to enhance soil desorption/diffusion of contaminants and thus enhance contaminant biodegradation. Additionally, naturally secreted biosurfactants may also serve to influence soil desorption/diffusion processes which are not accounted for in the conceptual model.

APPROACH

Biological treatment of contaminated soils and sludges associated with coal-tar derived processes has been evaluated by the co-authors through laboratory microcosms and a pilot-scale field plot. The results of this work imply that both the rate and extent of PAH soil reductions attributed to biodegradation may be directly related to the extent of PAH desorption from the soils and diffusion within the soil water matrix.

Data related to two separate studies are presented. One study relates to laboratory soil microcosms and the second to pilot-scale field work simulating land treatment. The focus of the studies performed was to evaluate the capability of soil biodegradation under proper environmental conditions (e.g., pH, temperature, nutrients) without the aid of chemical amendments (e.g., surfactants or supplemental organics).

Laboratory Soil Microcosms

The technical feasibility of biodegrading PAHs in contaminated soil from a Manufactured Gas Plant (MGP) site was evaluated in soil microcosm reactors. Two phases of work were performed. During one phase, the microcosms were loaded with 75 percent by weight contaminated MGP site soil and 25 percent uncontaminated soil known to contain PAH degraders. This uncontaminated seed soil was added to augment the soil microorganisms present, to dilute potentially toxic compounds which might be present, and to buffer the soil mixture. A total of 15 individual microcosms were established. Each microcosm consisted of a 400 ml glass beaker containing 60 grams of a soil mixture and a dedicated glass stirring rod. The microcosms were incubated at 35°C, moisture was controlled near 40 percent by weight (i.e., 80 percent of field capacity), and the pH remained near 7.6 for the study duration. Nitrogen and phosphorus were not specifically monitored for, but previous work with the seed soil showed that supplemental nutrient addition was not required to achieve PAH soil biodegradation. At each sampling event, three microcosm reactors were sacrificed for PAH analysis. Triplicate analyses were performed for statistical purposes. The triplicate samples were taken initially and at two, four, eight and twelve weeks of operation.

A second phase of the soil microcosm work examined the biodegradation of supplemental naphthalene applied to both contaminated MGP site soil and uncontaminated soil. The microcosms were operated and maintained similar to the first phase of work with the exception that 10 grams of a uncontaminated soil mixture was added which included 1 gram of seed soil. The naphthalene was added to the soil in each microcosm in a 0.1 ml solution of acetone containing 10 mg/ml naphthalene. At each sampling event, triplicate microcosm reactors were sacrificed for PAH analysis. Samples were taken initially and at weeks one, two, three and four during operation.

All PAH soil analyses were performed by EPA Method 8310 (HPLC) as specified in the third edition of SW-846 [18].

Pilot-Scale Bioremediation Test Plot

The second study cited involved the operation of a 12 ft. x 50 ft. pilot-scale bioremediation plot treating creosote-contaminated soil for approximately a 57 week period.

Contaminated soil was applied to achieve an initial benzene extractable content of approximately 4 percent by dry weight. Initially, agricultural manure equivalent to 10 tons/acre and agricultural fertilizer equivalent to 2 tons/acre were applied giving a C:N ratio ranging between 25:1 to 50:1. After approximately 57 weeks of treatment, the C:N ratio ranged between 15:1 to 20:1 indicating a large reduction in soil organic carbon compared to nitrogen, thus indicating biological activity. Agricultural lime, equivalent to 2 tons/acre, was initially added and this served to maintain the soil pH between 6 to 7 during the entire treatment period.

The bioremediation plot was initially loaded with contaminated soil in September, 1985, with operation being performed through October, 1985. Operation basically ceased from November through April due to cold weather. Operation resumed in May, 1986 and continued through October, 1986.

During operation of the treatment plot, soil moisture was maintained near 80 percent of the field capacity and tilling was performed at an 8 inch depth bi-weekly for mixing and aeration purposes. Triplicate composite samples were taken initially and at weeks 5, 20, 31, 35, 42, 46, 51 and 57 during the operating period. Week 20 corresponds to a sampling event in February, 1986. In addition, to moisture and pH as needed for operational monitoring purposes, the samples were also analyzed for PAHs by EPA Method 8310 [18].

PROBLEMS ENCOUNTERED

Due to the heterogeneous nature of the soils, replicate soils analyses for the same soil did exhibit some variability. Additionally, PAH volatilization was not measured, thus reductions in soil concentrations attributed to biological oxidation may be slightly overstated. However, these missing data are probably not critical due to the low volatility of PAHs as cited by the US EPA [5, 6]. Quantification of soil PAHs was also complicated by interfering compounds present in the sample extracts which produced a rising baseline which could have contributed to the wide variations in PAH soil concentrations which were measured.

RESULTS

Laboratory Soil Microcosms

Results of the laboratory microcosm study are given in Figures 2 and 3. Data plotted are averages of the triplicate samples analyzed.

Figure 2 illustrates a situation where no statistically significant PAH soil reductions were measured over a three month treatment period with the microcosms operated under the proper environmental conditions of pH, oxygen, moisture and nutrients. Data are presented for a summation of all sixteen PAHs as well as the individual ring groupings cited in Table 1. Water extracts of the soil showed no detectable PAH concentrations which agree with the premise that if PAHs do not desorb and diffuse into the bulk liquid phase, they are unavailable for biological oxidation.

The data given in Figure 3 further supports the desorption/diffusion hypothesis. Data is presented for the degradation in microcosm reactors of contaminated MGP site soil and uncontaminated soil both of which had been spiked with naphthalene added in an acetone solution. The acetone volatilized with the naphthalene left on the soil. As shown, the majority of the naphthalene applied to the uncontaminated soil was reduced within a one week period with less than detectable soil concentrations at week three. The naphthalene added to the contaminated soil was reduced to a level near what was originally measured in the soil before the naphthalene addition. Statistically, there is no difference between the baseline naphthalene soil concentration of approximately 26 mg/kg and the concentrations at weeks 1, 2, 3, and 4 for the MGP soil with naphthalene applied. These results imply that the freshly applied naphthalene was rapidly mineralized while the naphthalene associated with the original MGP soil was not susceptible to biological oxidation. Thus, the effect of soil aging appears to play a significant influence on PAH soil sorption and biological oxidation processes.

Pilot-Scale Bioremediation Test Plot

Figure 4 presents summary data for the pilot-scale test plot. The mean values given for the triplicate sample analyses show rather good reduction for all PAH ring groupings with total PAH reduced approximately 97 percent from an initial soil concentration of approximately 6,660 mg/kg to 176 mg/kg. The data also show that the fastest rate of soil reductions occurred within the first month of treatment with the soil concentrations somewhat leveling off after this. This leveling off between weeks 5 and 20 corresponds to cold weather operation. At week 31 (May, 1986), a second reduction in soil PAHs was measured.

In agreement with the previously presented hypothesis, the greatest extent of reduction occurred with the 2-, 3- and 4- ring compounds and relatively less for the 5- and 6- ring. Corresponding to the PAH ring groupings cited in Table 1, a summation of 2- and 3-ring PAHs were reduced from an initial mean soil concentration of 2,540 mg/kg to 6 mg/kg, 4-ring PAHs were reduced from 374 mg/kg. to 45 mg/kg, 5-ring total PAHs were reduced from 310 mg/kg to 88 mg/kg, and 6-ring total PAHs were reduced from 70 mg/kg to 37 mg/kg. These data do show significant reductions of all sixteen PAHs and document that the extent of biodegradation decreases with increasing ring number and molecular weight. This observation can be partially explained by the fact that the PAH aqueous solubilities decrease and the affinity for desorption from solids decrease as molecular weights (i.e. ring number) increase. These two factors are the primary reasons why the PAH mean half lives reported in the literature for land treatment of contaminated soil generally increase with increasing molecular weight [9,10].

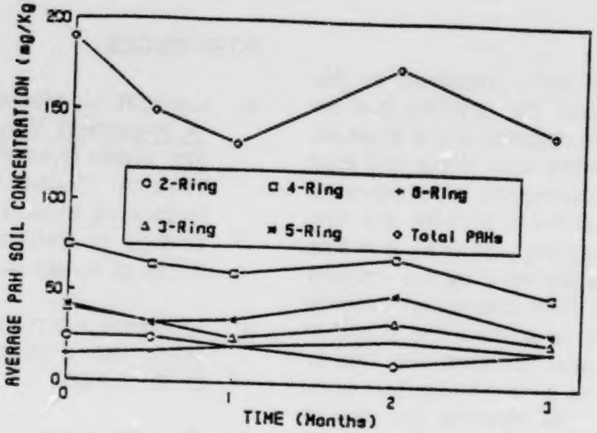


Figure 2. Laboratory Microcosm PAH Results
(3:1/Contaminated MGP Soil: Uncontaminated Seed Soil)

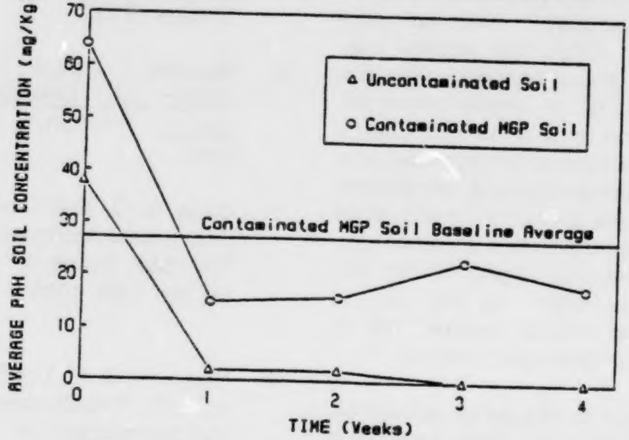


Figure 3. Degradation of Spiked-Additions of
Naphthalene in Soil Microcosms.

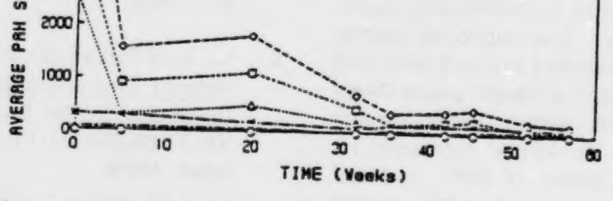


Figure 4. PAH Reduction in Pilot-Scale Bioremediation Test.

Summary

Comparison of the data presented in this paper begins to support the premise that for coal-tar related PAHs to degrade in soil systems, they must desorb from the solid matrix and exist in aqueous solution. During the initial period of treatment, desorption of PAHs from the soil may have been rapid, decreasing with time. It is also possible that enzymes secreted by the bacteria may serve to aid the PAH desorption process over time. Volatilization of some of the 2- and 3-ring PAHs may have also occurred with little or no volatilization of the 4-, 5- and 6-ring PAH compounds anticipated. This dynamic process of desorption/diffusion, volatilization and biological oxidation was operative until no further significant desorption of PAHs occurred as evidenced by no further reductions measured in PAH soil concentrations with time. While this premise may explain the observed phenomenon of PAH soil concentrations leveling off at certain concentration plateaus, it does not explain the mechanisms by which the PAHs become so incorporated into the soil material that desorption and subsequent biological oxidation does not occur. It also does not explain why treatment plateaus obtained vary from soil to soil. Perhaps aging of the soil material may have an effect, as well as the characteristics of the coal-tar source that is associated with the contaminated material.

The data presented in this paper should be considered very preliminary in nature; however it does begin to support the complexity of the interactions between PAHs and soils and the effects of such interactions on the susceptibility of PAHs to biodegradation in soil systems. For this reason, future research work should focus on better understanding of the mechanisms affecting such interactions. Specifically, the effects of physical/chemical soil and waste characteristics on the mechanisms discussed should be investigated. Through a better understanding, biological treatment of PAH contaminated soils and sludges can be applied in a scientifically sound and acceptable manner. This especially relates to the issue of risk assessment in that if soils and sludges are bioremediated to levels where PAHs are so bound to and incorporated within the soil aggregates, they may no longer represent an environmental risk in terms of both leachate migration to groundwaters and public health exposure issues.

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DESIGN CONSIDERATIONS FOR FIXED-FILM, AEROBIC, MICROBIOLOGICAL DEGRADATION OF HAZARDOUS WASTE

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ABSTRACT

Microbiological processes are currently being investigated as potential treatment methods for the remediation of contaminated waters at hazardous waste sites. There is sufficient information available documenting that biodegradation of hazardous wastes is a feasible treatment method, however, many details of process design still need to be determined.

This paper describes a study where two fundamental design questions were addressed: 1) What is the minimum depth of the material supporting the bacteria required for the removal of a contaminant? and 2) What is the effect of hydraulic loading on bacterial removal efficiency? The study was conducted in the laboratory using fixed-film biological reactor columns. Pentachlorophenol (PCP) and other chlorophenols were used as the test contaminants. Dechlorinated Philadelphia tap water was used as the source water. The concentration of the contaminants added to the source water ranged between 200 and 1000 µg/l. The columns were packed with Ottawa sand (20-30 mesh). Incremental depths of sand were used for individual columns. The columns were operated in a downflow mode and the flow rates through the columns were varied from 0.5 gpm/ft^2 to 2 gpm/ft^2. A high percent removal of the contaminants was achieved. The data indicate that biological activity through a biofilm process in a small column for the removal of trace amount of pollutants is possible, thereby allowing for the complete cleanup of water from a contaminated area.

INTRODUCTION

Microbiological processes have been extensively studied and used for the treatment of industrial and domestic wastes. The same processes may be adapted for the remediation of contaminated ground water from hazardous waste sites. This adaptation is necessary because the design is for a fundamentally different situation. With conventional industrial waste or domestic waste treatment, the water to be treated is continuously flowing, necessitating the biological unit operation to be run continuously all year long. A contaminated ground water will usually be of a finite volume, allowing for intermittent or seasonal treatment as well as permitting the luxury of being able to control the hydraulic loading rate to the system.

Another important difference between the two situations is the nature of the material to be treated. With the conventional treatment process the material to be degraded is usually available as a primary carbon source and usually occurs in mg/l quantities. The presence of the material as a primary carbon source will allow a shorter acclimation period and will permit a much shorter start-up time. With the water from a hazardous waste site, the contaminants may be only present in µg/l quantities, which will not be a sufficient carbon supply to sustain the cells. Therefore, a primary carbon source will be required, and should be present in the ground or surface water as dissolved organic matter. The primary carbon source needs to be in a quantity such that the microbial cells can sustain themselves, however, an acclimation period - (a time where the microorganisms adapt their metabolisms to the breakdown of specific contaminants) may be necessary.

Because of the differences outlined above, conventional designs for biological treatment systems may not be able to handle the special requirements for a hazardous waste site remediation. However, an attached/entrapped growth system may be modified for the special needs of a hazardous waste site. The ability of microorganisms to attach and colonize a surface may afford them adequate contact time with the contaminants, access to necessary primary nutrients and, under some circumstances, protect them from toxic conditions. The term biofilm (or fixed-film) is used to describe the attached microorganisms. The biofilm process can be brought about either _in situ_ or as an above-ground pump and treatment scheme, and either alone or in conjunction with other treatment process operations.

PURPOSE

In this study two fundamental design questions were addressed: 1). What is the minimum depth of biofilm support material required for the removal of a contaminant? and 2). What is the effect of hydraulic loading rate on bacterial removal efficiency?

The study was conducted in the laboratory using "fixed-film" biological reactor columns. Pentachlorophenol (PCP), 2,4,6 trichlorophenol and 2,4 dichlorophenol were used as the test contaminants. These compounds were chosen because of their documented biodegradability, their occurrence as contaminants in both soil and water, their nonvolatile nature and their ability to be detected in µg/l (ppb) quantities.

APPROACH

Apparatus

Two types of column systems were used. For the preliminary (Phase I) studies, borosilicate glass columns were

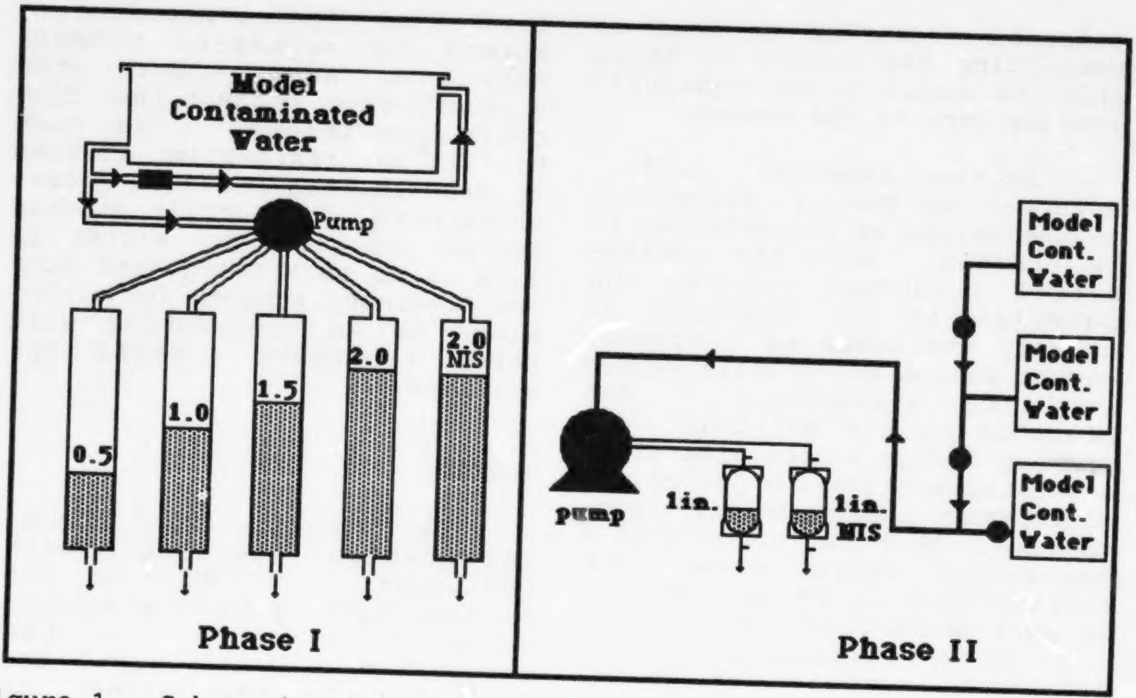

Figure 1. Schematic of the experimental apparatus. For the phase I studies 0.5 ft. incremental depths were used. One inch depths were used in the phase II studies. N I S - No Initial Seed.

used. These columns were 3.0 feet in length and had a 2.5 inch internal diameter. They were initially cleaned by acid washing (50 % v/v HCl) and rinsed five times with deionized water. After air drying, they were autoclaved for 15 minutes @ 121°C. The columns were covered with aluminum foil in order to prevent any light induced reactions. Figure 1 is a schematic of the experimental apparatus.

Ottawa sand (20-30 mesh) was used to pack the columns. The sand was initially rinsed five times with deionized water and allowed to air dry. After drying, the sand was autoclaved for 15 minutes @ 121°C. After drying, the sand was aseptically added to individual columns at incremental depths of 0.5 ft. to 2.0 ft.

For the Phase II studies, smaller columns were used. These smaller columns were made of teflon, and were 4.75 inches in length and had an internal diameter of 1.6 inches. The columns were initially acid-washed (50 % v/v HCl) followed by 5 deionized water rinses. The columns were allowed to air dry and were then autoclaved for 15 minutes @ 121 °C. Sand, prepared as described above was added to the individual columns to a depth of one inch. The columns were also covered with aluminum foil when in use.

A Cole Parmer peristaltic pump was used to transport the contaminated water. This pump was capable of delivering water to each column at rates ranging from 0.5 to 2.0 gpm/ft^2. Silicon tubing was used to connect the pump to the columns. All other tubing or fittings were made of teflon, glass or stainless steel.

Model contaminated water for all experiments was made by passing Philadelphia Tap Water through Calgon Filtrasorb F400 Activated Carbon to remove chlorine. The effluent from the activated carbon was checked daily for chlorine removal (Hach field kit) and the influent and effluent to the column was monitored for total organic carbon (nonpurgeable organic carbon) to insure an adequate primary carbon source. The water was stored in 50 gallon Nalgene tanks and allowed to equilibrate to ambient temperature (20-23°C) before use. These tanks were covered to prevent light infiltration.

The contaminants used were PCP, 2,4,6 trichlorophenol and 2,4 dichlorophenol from Aldrich Chemical (Milwaukee, Wisconsin). All three compounds were added to the reservoirs to give a final concentration between 500 and 1000 µg/l of each compound.

Seed Organisms

The bacteria used for the initial inoculation of some of the columns consisted of a suspension containing an *Arthrobacter* (ATCC 33799) and five isolates obtained from soil from the EPA Region III Havertown, PA PCP Superfund site. These isolates demonstrated the ability in laboratory culture to use PCP as a sole carbon source. The six bacteria were individually grown in batch culture for seven days at 25° C with shaking in a mineral salts medium amended with 500 µg/l PCP. Five grams of mud from the Schuykill River in Philadelphia, PA were also inoculated into the PCP-mineral salts medium in the same manner.

Startup and Operation

For the Phase I studies, a total of five columns were used. Four columns filled with sand at 0.5 ft incremental depths were inoculated with the Seed bacteria in the following manner: The columns were initially filled with contaminated water. Five ml from each batch culture (35 ml total) were aseptically added to each column. The final density of each culture was between 2 x 10^5 and 1 x 10^7 CFU/ml. Each mixture in each column was then recirculated through each column operated in a down-flow mode for twenty-four hours. Next, the columns were allowed to sit undisturbed for twenty four hours. The columns were then ready to go on-line. A fifth column packed with the same depth of sand as the deepest seeded column was not seeded, but was treated in the same manner otherwise. The columns were operated in a downflow mode. For the phase II studies the columns were initially started and then operated in a similar manner.

Analytical Methods

Three parameters, dissolved oxygen (DO), pH, and temperature were determined for the influent and effluent of each column each day. DO was monitored using a YSI Model 57 portable oxygen meter. pH was monitored using an Orion Research Model 399A pH meter.

Organic Analyses

The concentrations of the chlorophenolic compounds were measured using a Varian High Pressure Liquid Chromatograph (HPLC). The HPLC was used with acetonitrile-water as the mobile phase, and a Varian MicroPak MCH-10 reverse phase column as the stationary phase. A 1 ml sample volume was used and the compounds were characterized with a UV detector at a wavelength of 254 nm. A detection limit of 50 µg/l was obtained for each compound.

Total organic carbon (TOC) analysis for non-purgeable organic carbon (NPOC) was performed on a Xertex, Dohrman Carbon Analyzer (DC-80) according to Standard Method (1) procedures.

Heterotrophic Counts

Instantaneous grab samples were collected in sterile 250 ml Nalgene polypropelene bottles at the influent and effluent of each column. Serial dilutions were made in sterile physiological saline, and 0.1 ml aliquots were spread-plated onto R2A agar (3) in duplicate. The plates were incubated in the dark for seven days at 25° C.

PROBLEMS ENCOUNTERED

One problem that was encountered was the development of an acclimated PCP degrading population in the source water reservoirs. This was overcome by weekly draining and manually cleaning and scrubbing of the tanks.

Another problem concerned the effect of temperature on acclimation time. Low temperatures (< 20° C) inhibited the establishment of an acclimated microbial population within the columns. This was overcome by running all experiments between 20 and 23° C.

RESULTS

Phase I Studies

Results from the Phase I studies showed that after an initial acclimation period, complete removal of PCP and 2,4,6 trichlorophenol was obtained at all depths at a flow rate of 0.5 gpm/ft^2. 2,4 dichlorophenol was completely removed from columns with depths of sand 1.5 ft and greater.

Seeding of the columns with acclimated organisms also did not appear to have a positive influence on removal of the compounds. Removal of the compounds occurred at about the same times in both the seeded and unseeded 2.0 ft. column: approximately 150 hours for PCP, 170 hours for 2,4,6 trichlorophenol and 200 hours for 2,4 dichlorophenol.

The other parameters measured during the course of the Phase I experiments showed the temperature for the run ranged between 21 and 23° C, the pH varied between 7.5 and 7.7 for both the influent and effluent of all columns, and the

D.O. depletion between the influent and effluent averaged about 2.0 mg/l. The heterotrophic plate counts from the influent to all the columns ranged from 4.0 x 10^4 to 2.4 x 10^5 CFU/ml (colony-forming-units). The counts from the effluent from all of the columns ranged from 2.0 x 10^4 to 1.4 x 10^5 CFU/ml. The influent consistently had higher counts than the effluent.

Two interesting observations were made during the phase I study. Mechanical difficulties were experienced which caused the system to be shut down for short periods during a preliminary run, resulting in a 'pulsing' effect of the contaminated water onto the columns. It was observed that this action appeared to aid in the establishment of an acclimated population within the columns. It was also noted that in all of the columns a 'biofilm' was observed that extended approximately $^1/_4$ inch in depth in the sand from the top of the column. The 'biofilm' was a brownish-olive green in color and appeared to be evenly distributed over the $^1/_4$ inch depth.

Because of the results in the Phase I study which showed that apparent removal of the compounds was possible with six inches of sand and that the biofilm only penetrated approximately $^1/_4$ inch, a smaller depth of sand (1 inch) was used for the next series of experiments (phase II).

Phase II Studies

Table 1 shows the length of time required to establish an acclimated culture for the degradation of the three chlorophenolic compounds in an inch depth of sand. As can be seen from the table, there was no advantage to the seeding process, as both columns behaved identically. PCP was the compound most rapidly adapted to degradation by the populations within the columns. 2,4,6 trichlorphenol and 2,4 dichlorophenol were more slowly acclimated for.

The pattern of TOC removal (measured as NPOC), as shown in Table 1, by the populations in both columns was erratic and varied from day to day. This phenomena was consistently observed for all experimental runs for all operating conditions and is in agreement with observations made in other studies (2).

The effect of hydraulic flow rate on percent removal of contaminant was next studied. These runs consisted of operating the system for seven days at the designated flow rate with daily sampling of the influent and effluent. Seven days was chosen because of the observation that equilibrium removals were obtained within the columns between three and five days. The flow rates used were 0.5, 1.0 and 2.0 gpm/ft^2.

Figure 2 illustrates removal efficiencies vs flow rate for the three compounds. Each point represents the average removal efficiency at equilib-

Table 1. Percent Removal (influent vs effluent) for the three chlorophenolic compounds used in the Phase II study. S- seeded; NIS- no initial seed; * - No apparent removal.

Elapsed Time (hrs.)	Percent Removal of 2,4 dichlorophenol		2,4,6 trichlorophenol		PCP		NPOC	
	S	NIS	S	NIS	S	NIS	S	NIS
0	18	5	*	11	*	*	49	*
51.5	*	*	5	*	*	*	16	*
95.5	4	*	23	*	13	15	6	34
146.0	*	1	19	6	53	32	*	6
193.5	2	*	*	*	49	47	*	11
215.0	24	10	29	32	47	60	13	5
239.0	31	17	*	*	54	71	28	26
260.5	11	*	*	27	54	71	42	27
287.5	*	*	32	34	71	92	57	*
308.5	*	10	*	35	68	92	9	*
336.5	*	28	*	54	74	90	9	27
384.0	*	15	24	17	72	92	45	22

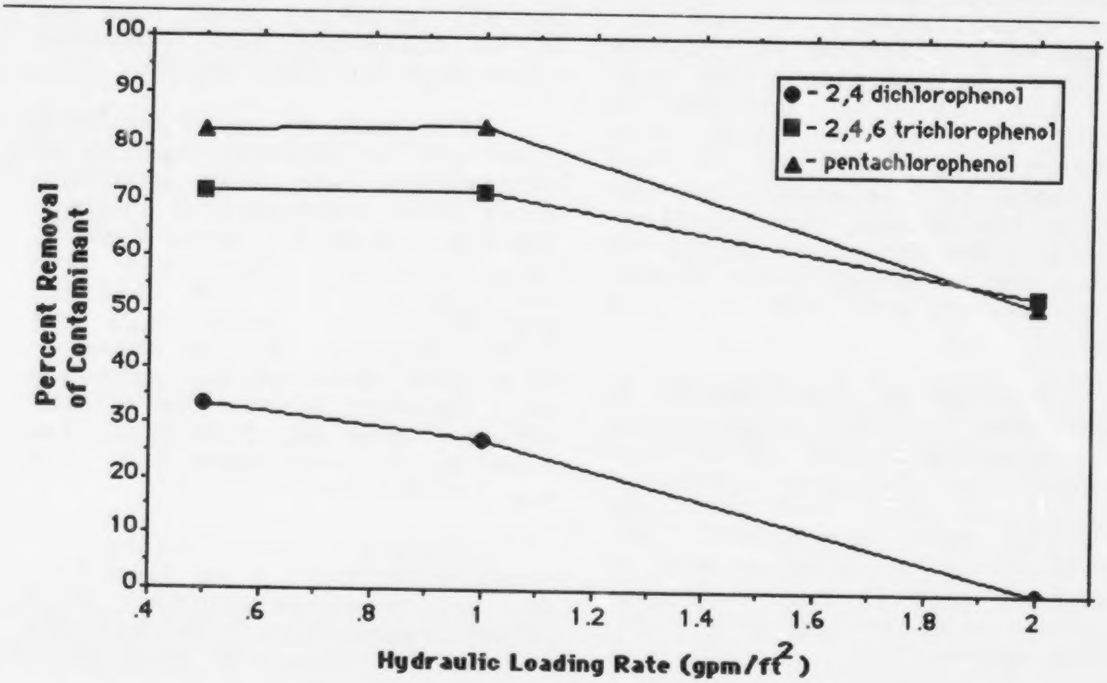

Figure 2. Percent removal of each chlorophenolic compound vs hydraulic loading rate (gpm/ft^2).

rium which was at least 72 hours for both columns. The removal efficiency for all three compounds did not differ at loading rates of 0.5 gpm/ft^2 but decreased at a loading rate of 2.0 gpm/ft^2. These results suggest that through an increase in the depth of biofilm support material, high loading rates can be handled and complete removal of the contaminants is possible.

The data also show a consistent pattern of PCP being the contaminant most readily degraded, followed by 2,4,6 trichlorophenol and 2,4 dichlorophenol. These chlorophenolic compounds have proven to be biodegradable by both pure cultures and mixed natural microbial populations and complete mineralization of the contaminants was observed in most situations (4). However, in this case the rate of disappearance of the compounds varies suggesting an effect by loading rate as well as other contributing environmental factors. This factor will prove to be important for design at hazardous waste sites, because in almost all situations the waste is composed of a variety of compounds. The results from this study indicate that even though the compounds may be from the same characteristic group, in this case the chlorophenols, different removal rates at all depths and with all loading rates were observed. This factor will entail designing the biological system based on 'target compounds,' or more ideally using the biological process in conjunction with other physical-chemical operations to selectively remove all contaminants of interest.

The results from this study indicate that there is the potential for promoting biological activity through a biofilm process in a very small area for the removal of trace amounts of contaminants, thereby allowing for the complete clean-up of a contaminated area. Work is continuing to establish a more quantitative relationship between flow rate, depth of sand and microbiological activity within the depth of sand on the removal efficiency of trace amounts of contaminants.

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APPLICABILITY OF STEAM STRIPPING TO ORGANICS REMOVAL FROM WASTEWATER STREAMS

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ABSTRACT

In the past five years the U. S. Environmental Protection Agency has studied the effectiveness of steam stripping as a treatment technique for removing organics from aqueous waste streams. This paper presents the data obtained from field tests of steam strippers at seven industrial faciliteis. The effectiveness of steam stripping for removing different types of organics from wastewaters is discussed.

INTRODUCTION

Two components of the Hazardous and Solid Waste Amendments of 1984 provide incentives to industry to reduce the organic contentof wastes. This can be done using organic removal treatment technologies, such as steam stripping. The Amendments require that the U.S. Environmental Protection Agency (USEPA) develop land disposal restrictions for hazardous wastes. These restrictions are intended to protect human health and the environment from releases of toxic compounds into the groundwater or to the air from land disposal facilities. The restrictions included limitations on the concentration of hazardous constituents in land disposed wastes. In addition, the Amendments require that emissions of volatile organics from hazardous waste treatment, storage and disposal facilities (TSDF) be reduced. Emissions reductions are intended to minimize the air pollution problems, such as ozone formation, which result from TSDF operation.

Wastewaters form a large percentage of the hazardous waste streams generated in the United States. For example, in 1981, 13.7 billion gallons of the 14.6 billion gallons, or 92%, of the hazardous waste disposed of in the nation went to deep-well injection or surface impoundments - disposal processes that are typically used for liquid wastes (1). Of the 398 million gallons of solvent (i.e. F001-F005) wastes disposed of in 1981, 266 million gallons, or 65%, were aqueous streams contaminated with less than 1% organics or solids (2).

The Agency is also studying ways to reduce emissions from industrial and municipal wastewater treatment facilities under the Clean

Air Act. Since open storage tanks and activated sludge and other aerated treatment processes are commonly used for managaement of organics in wastewaters, the potential exists for significant emissions from these facilities. Plants D, F and G in this paper were sampled by the USEPA as part of this program.

A number of treatment technologies have been used to remove organics from wastewater streams. These include steam stripping, biodegradation, carbon adsorption, solvent extraction and chemical destruction techniques, such as UV/ozonation. Steam stripping offers several advantages over the other available technologies. It can be used to recover the organics separated from the stream. It performs well in removing halogenated aliphatics; compounds that are not readily removed by carbon adsorption. And, it does not usually require the solvent recovery steps inherent in solvent extraction. For these reasons, steam stripping is expected to see increased use in wastewater cleanup.

This paper provides a summary of the results from seven field tests that have been performed by the USEPA to determine the effectiveness of steam strippers being used for wastewater treatment at industrial facilities. The results demonstrate the wide variety of organic compounds which this technology can efficiently remove from aqueous waste streams.

Steam Stripping

Stripping is a physical separation unit operation in which dissolved compounds are transferred from a liquid into the gas phase. The driving force for mass transfer is provided by the concentration gradient between the two phases. In steam stripping, live steam is used as the gas phase. The steam both heats the liquid, which enhances the rate of mass transfer, and carries the volatilized compounds away from the liquid (3).

Steam stripping can be performed in the batch or continuous mode. In the batch process, waste is charged to a boiler and steam is injected directly into the waste. The injection of live steam both heats the waste to volatilize low boiling components and creates turbulence in the waste, thus increasing the rate of volatilization. The gases which are condensed from a steam stripper will contain water along with the more volatile organic components of the waste in the form of a two phase mixture. This mixture is decanted and the organic component is drawn off for reuse or disposal. In a continuous steam stripping column, as shown in Figure 1, waste flows down a column while steam flows up. The column is designed to promote heat transfer from the steam to the waste, to cause turbulence in the waste and to create a large waste surface area. All of these properties promote transfer of volatile components from the waste to the gas phase. Different liquid-vapor equilibria exist in the column, with the highest relative concentration of the most volatile components found at the top. The separation of different volatile constituents may be enhanced by refluxing a portion of the condensate.

Steam stripping is generally used to separate insoluble or slightly soluble compounds from water. These compounds are readily stripped because they have a large air to water equilibrium coefficient which increases as the temperature

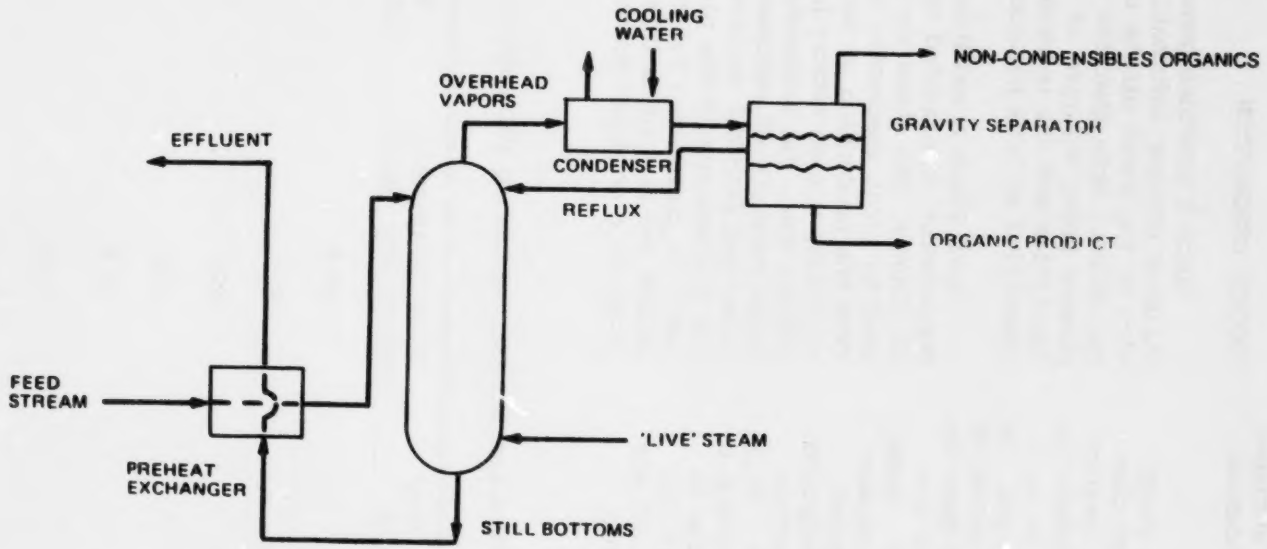
NON-CONDENSIBLES ORGANICS
COOLING WATER
OVERHEAD VAPORS
GRAVITY SEPARATOR
EFFLUENT
CONDENSER
REFLUX
ORGANIC PRODUCT
FEED STREAM
'LIVE' STEAM
PREHEAT EXCHANGER
STILL BOTTOMS

Figure 1. Steam stripper schematic.

of the waste is raised by the steam. In addition, a high percentage of the mass of the solvent in the condensate will be in the organic phase; only a small portion of the stripped organics are left in the condensed steam (4).

The aqueous phase of a steam stripper's condensate must be disposed of, however, and this requirement must be carefully considered in deciding whether stripping is an appropriate recycling technique. In a few instances, the small amount of water need not be separated from the organic phase and the entire condensate can be recycled (5). Generally, however, the aqueous condensate must be treated to a point where it can meet permit conditions upon discharge to either surface waters or a municipal sewer. While this can be accomplished through a separate process, the problem is usually handled by recycling the aqueous condensate to the influent stream of the stripper. This requires a steam stripping unit that is oversized to handle the additional load.

PROCESS DESCRIPTION

Table 1 provides general steam stripper process information for each of the seven plants sampled by the USEPA. Note that the waste streams being stripped at these facilities are not necessarily classified as RCRA hazardous wastes.

Both Plant A and B manufacture mono-carbon chlorinated solvents. At Plant A, the steam stripper is used to treat wastewater generated from the production of methylene chloride, carbon tetrachloride and chloroform. The wastewater at this plant consists of equipment wash water and rainfall collected from diked areas around the plant. Wastewater is pretreated for removal of solids and any immiscible organic phase in a decanter prior to strip-

Table 1. Selected steam stripper operating parameters.

Plant Identifier	Wastewater Flow Rate (l/min)	Volatile Organic Loading Rate (kg/l)	Feed/Steam Ratio (kg/kg)
A	41.5	14.6	9.6
B	21.0	4.6	10.5
C	852	292	28.8
D	2,390	286	NA
E	499	19.0	14.7
F	110	5.29	7.1
G	30.5	0.395	1.4

NA - Not available.

ping. The stripper column is packed with 2.5 cm (1-inch) saddles and processes 42 l/min (11 gpm). The stripper effluent, after cooling by a heat exchanger, enters a holding tank. If the organics analysis of this effluent meets NPDES discharge limits, it is pH adjusted and discharged to a river. Condensate from stripping is phase separated in a decanter. The aqueous phase is returned to stripper feed holding tank and the organic phase is recycled to the manufacturing process (5).

Facility B is a chemical manufacturing plant which produces a number of chemical intermediates that are used by the cosmetics, chemical and agricultural industries. The facility operates several processes including a methyl chloride steam stripping process. The waste routed to this steam stripper consists of methylene chloride, water, salt and organic residue. Feed is pumped from storage tanks through a preheat exchanger to the top of the stripper at approximately 20 l/min (5 gpm). The stripping tower is 20 cm (8-inches) in diameter and contains 3.3 meters (10 feet) of 1.6 cm (5/8-inch) Pall rings. The treated effluent flows through a heat exchanger and ultimately to the local publicly-owned treatment works (POTW). The overhead vapors are liquified in a water-cooled condenser and separated by gravity in a decanter. The aqueous phase is recycled to the top of the stripping column while the lower layer of methylene chloride is stored for reuse (6).

Plant C produces 1,2-dichloroethane (EDC) and vinyl chloride monomer (VCM). Wastewaters from the EDC/VCM production operation and from other parts of the plant, including storm water runoff, are treated by steam stripping. The feed rate to the stripper is in the range of 760 to 950 l/min (200-250 gpm). There is no pretreatment of this stream and the feed stream contained 1.4 g/l filterable solids during USEPA field tests. As a consequence, the column contains trays instead of packing and both the column and heat exchangers must be backwashed periodically. The effluent from the steam stripper passes through a heat exchanger and is then sent to a wastewater treatment system for treatment of residual, nonvolatile organics. The condensate could be phase separated by decanting, but at this facility the complete aqueous/organic mixture is recycled directly to the manufacturing process (5).

Plant D is a chemical manufacturing facility producing chlorinated hydrocarbons. Steam strippers treat wastewater generated by various chlorinated hydrocarbon production units operated at the facility. Scrubber blow down streams, aqueous reactor equipment streams and pad water are collected from around the facility and pumped to settling tanks prior to stripping. The one exception is wastewater from the VCM production unit which is pumped directly to the stripper. In the settling tanks insoluble organics are separated from the aqueous stream, which is then fed to the strippers. Total suspended solids concentrations in the feed were low, ranging from 6.4 to 65.6 mg/l over three days. Two wastewater strippers operated in parallel are used for treatment and waste reclamation as NPDES treatment units. Approximately 2,400 l/min (650 gpm) of wastewater enter the stripper.

Plant E is an explosives manufacturing plant with process wastewater streams that are predominately red water and white water. These streams pass through decanters where the oils are separated from the process. There is no other pretreatment of the stream and some fouling of the feed preheater results, although plant personnel reported less than one percent down time for the unit. The steam stripper is packed with 2.5 cm (1-inch) diameter stainless steel rings and had a feed rate of approximately 500 l/min during USEPA tests. The effluent from the steam stripper passes through a heat exchanger and then through one of two carbon adsorption beds. The carbon served as a polishing step removing residual organics from the waste stream. After pH adjustment, the effluent stream is discharged to a river. The condensate is phase separated in a decanter. The aqueous phase is returned to the stripper feed tank, while the organic phase is routed to an organics slop sump (5).

Plant F is a chemical manufacturing facility which uses steam stripping for treatment and material reclamation from wastewater streams generated by both production units in one process area of the plant. Toluene is the principal compound being recovered. Waste streams are pretreated by either a primary decanter (for toluene removal) or an evaporator (for solids thickening) and then flow to the steam stripper feed decanter where additional separation of insoluble organics is obtained. The flow rate to the steam stripper is 60 to 150 l/min (15-40 gpm). Total suspended solids concentration ranged from nondetectable (<4.0 mg/l) to 8.5 mg/l during USEPA field tests. The column is 2.5 feet in diameter and contains 20 sieve trays. The condensate from the first stage condenser is recycled to the feed decanter. The steam stripper bottoms are discharged through the plant's process sewer to the plant's on-site wastewater treatment plant.

Plant G is an agricultural chemical manufacturing facility. The primary source of wastewater for this plant's water layer steam stripper is a jet collection system which is used to pull a vacuum on various process refining stills and reactor recovery stills. A scrubber decant pot and periodic reactor washes also contribute to wastewater in the stripper feed. The wastewaters are pumped to a decanter tank for liquid organics and sludge separation and removal. Flow rates to the steam stripper averaged 31 l/min (8 gpm) during the test period. Total suspended solids content of the feed for this stripper was not monitored. The stripper column is 60 inches in diameter and contains 14 Glitsch valve trays spaced one foot apart. Nitrogen is used to maintain the column pressure at 5 pounds per square inch. Condenser overheads are pumped back to the jet collection pot. The stripper effluent is discharged through the facility's process sewer to the wastewater treatment plant.

STRIPPER PERFORMANCE

Table 2 presents performance data for each of the 7 strippers discussed above. Results are based on one of three days of collecting data at each facility.

The performance data demonstrates that continuous steam stripping achieves efficient (>95%) removal for a range of compounds, typically yielding concentrations of individual compounds of less than 1.0 ppm. (An exception, Plant E, found it more cost-effective to achieve these levels by a combina-

Table 2. Steam stripper organic removal effectiveness.

Pollutant	Inlet Concentration ppmw	Outlet Concentration ppmw	Removal wt. %
Plant A			
Chloromethane	33	<0.005	>99.98
Methylene chloride	4,490	<0.011	>99.999
Chloroform	1,270	<0.006	>99.999
Carbon tetrachloride	55	<0.005	>99.99
Trichloroethylene	5.6	<0.005	>99.9
1,1,2-Trichloroethane	5.3	<0.005	>99.9
Total VOC	5,860	<0.037	>99.999
Plant B			
Methylene chloride	3,600	<0.19	>99.99
Chloroform	52	5.3	89
Carbon Tetrachloride	<2.3	<0.17	>92
Total VOC	3,654	<5.6	>99.8
Plant C			
1,2-Dichloroethane	5,630	0.097	99.998
Chloroform	271	9.6	96.4
Benzene	0.27	<0.01	>96
Carbon tetrachloride	1.7	<0.01	>99.4
Chlorobenzene	0.38	<0.01	>97
Chloroethane	9.6	<0.01	>99.89
1,1-Dichloroethane	11	<0.01	>99.91
1,1-Dichloroethene	4.7	<0.01	>99.8
1,2-Dichloroethene	8.9	<0.01	>99.8
Methylene chloride	1.2	<0.01	>99.1
Tetra-chloroethene	1.4	<0.01	>99.2
1,1,2-Trichloroethane	7.5	<0.01	>99.8
Trichloroethene	4.8	<0.01	>99.7
Vinyl chloride	8.4	<0.01	>99.8
Total VOC	5,960	<9.8	>99.8
Plant D			
1,1-Dichloroethene	25.4	<0.041	>99.84
1,1-Dichloroethane	61.7	<0.045	>99.93
trans-1,2-Dichloroethane	68.5	<0.227	>99.67
Chloroform	181	1.75	99.03
1,2-Dichloroethane	974	2.15	99.78
1,1,1-Trichloroethane	44.6	<0.051	>99.89
Trichloroethene	45.0	<0.078	>99.83
1,1,2-Trichloroethane	156	0.188	99.88

Table 2. (Continued)

Pollutant	Inlet Concentration ppmw	Outlet Concentration ppmw	Removal wt. %
Plant D (continued)			
Tetrachloroethene	162	<0.171	>99.89
Total VO	1994	4.90	99.75
Plant E			
Nitrobenzene	505	41.0(<0.8)[a]	91.8(>99.8)[a]
2-Nitrotoluene	78	2.4(<0.8)	96.9(>98.9)
4-Nitrotoluene	51	4.4(<0.8)	91.4(>98.4)
Total VOC	634	47.8(<2.4)	92.4(>99.6)
Plant F			
Benzene	1.84	0.0020	99.89
Chlorobenzene	1.47	0.003	99.80
1,2-Dichlorobenzene	3.04	0.005	99.84
1,3-Dichlorobenzene	3.51	0.002	99.94
1,4-Dichlorobenzene	3.29	0.003	99.92
Ethylbenzene	2.45	0.002	99.92
Toluene	779	0.283	99.96
O-xylene	1.00	0.002	99.80
M-xylene	1.53	0.002	99.87
P-xylene	1.00	0.002	99.80
Total VO	798	0.305	99.96
Plant G			
Benzene	5.06	0.012	99.62[b]
Toluene	1.07	0.007	98.94[b]
Ethyl Benzene	1.46	0.005	99.44[b]
Isophorone	1.04	0.026	96.02[b]
Naphthalene	12.0	0.026	99.66[b]
5-Ethyl-1,2-Methylpyridine	96.4	9.18	84.54[b]
1,2,3,4-Tetrahydronaphthalene	76.7	0.789	98.33[b]
Acetophenone	9.91	0.127	97.91[b]
2-Methyl-1,3-Cyclopentanedione	12.1	0.127	98.29[b]
Total Organics	225	10.3	92.45[b]

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[a] For Plant E, values shown in parentheses are effluent concentrations and removal efficiencies for the treatment of the influent stream by a combination steam stripping followed by carbon adsorption.

[b] Percent removal based on mass flow rates of organics in stripper influent and effluent streams. Average flow rates of influent and effluent streams were 1,831 kg/hr and 2,973 kg/hr, respecitively.

tion of steam stripping and carbon adsorption.) The first four plants were treating wastewater streams contaminated with halogenated aliphatics, with individual compound initial concentrations as high as 0.56%. These compounds have Henry's Law Constants, H, ranging from 4.3 x 10-4 to 1.2 x 10-2 atm-m3/mole. Halogenated aromatics having similarly high H values were also removed effectively, as shown by the data presented for chlorobenzene and dichlorobenzene at Plant F.

Plants E, F and G treat non-halogenated aromatics, ketones and other compounds which are more water soluble and have lower Henry's Law Constants than the above halogenated organics. Good removal efficiencies were also achieved for these compounds. Benzene, toluene, xylene and ethyl benzene were removed with greater than 99% efficiency, while naphthalene and 1,2,3,4-tetrahydronaphthalene are removed with better than 98% efficiency.

Plant E achieved greater than 90% reduction of nitrobenzene and nitrotoluene using steam stripping, with overall removal efficiencies of greater than 98% for these compounds when carbon adsorption was used for polishing. The nitro group on the aromatic ring suppresses the Henry's Law Constant by over an order of magnitude for these compounds compared to halogenated organics, requiring increased energy for their removal. This led Plant E to decide to operate a treatment system which utilized carbon adsorption for final effluent polishing prior to discharge. Despite the relatively low H value for these chemicals (2 to 7 x 10-5 atm-m3/mole), steam stripping is still practical since the low solubility of nitrobenzene and the nitrotoluenes, 1,900 mg/l and approximately 600 mg/l, respectively, allow a large percentage of these compounds to be separated by decanting from the aqueous condensate produced by the stripping process. Ninety-four percent of the stripped nitrobenzene was removed from the condenser, while over 98% of the nitrotoluene isomers were removed.

CONCLUSIONS

Steam stripping can achieve better than 95% removal efficiency for a range of organic compounds which are insoluble or slightly soluble in water. Effluent concentrations of less than 10 ppm, and for most compounds less than 1 ppm, can be obtained using steam stripping. Polishing of the steam stripper effluent using carbon adsorption may be the most cost-effective means of achieving these low concentrations for the less volatile compounds in the group represented by these seven tests. The presence of solids in wastewaters can foul steam strippers and therefore it is generally advantageous to remove these solids before stripping. Decanters are typically used to achieve solids removal and concurrently remove any insoluble organics which will also interfere steam stripper operation.

ACKNOWLEDGEMENT

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

SITE PROGRAM DEMONSTRATION OF THE CF SYSTEMS INC. ORGANICS EXTRACTION UNIT

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ABSTRACT

The Superfund Innovative Technology Evaluation (SITE) Program demonstration of the CF Systems organics extraction technology was conducted at the New Bedford Harbor Superfund site in Massachusetts. The demonstration was conducted concurrently with pilot dredging studies managed by the U.S. Army Corps of Engineers, from which samples of contaminated harbor sediments were obtained for use in the demonstration. Several tests were conducted on a trailer-mounted, pilot-scale unit to obtain specific operating, analytical, and cost information that could be used in evaluating the potential applicability of the technology to New Bedford Harbor and other Superfund sites. The primary objective of this demonstration was to evaluate the developer's treatment goals for extracting PCBs from harbor sediments. Secondary objectives included an evaluation of (1) the unit's performance in terms of extraction efficiency and a mass balance, (2) system operating conditions, (3) health and safety considerations, and (4) equipment and system materials handling problems.

CF Systems achieved an overall PCB concentration reduction over 90 percent for sediment samples that contained 350 ppm and 2,575 ppm. The unit generally operated within specified conditions for flowrates, pressure temperature, pH and viscosity. Deviations from operating specifications could not be correlated to changes in extraction efficiency. No significant releases of pollutants to the atmosphere or surrounding area soils occurred. Results of the demonstration tests show that the CF Systems technology is capable of reducing the PCB content of contaminated sediment by greater than 90 percent without a risk to operating personnel or the surrounding community. This information will assist in the engineering design and costing of a commercial scale unit at New Bedford Harbor in addition to identifying other sites where the technology may be economically applied.

INTRODUCTION

Through the Superfund Innovative Technology Evaluation (SITE) program, the U.S. Environmental Protection Agency (EPA) is assisting technology developers in the development and evaluation of new and innovative treatment technologies. The SITE program objective is to enhance the commercial availability and use of these technologies at Superfund sites, as an alternative to land-based containment systems that are used most often at Superfund sites. Part of the SITE program involves field demonstrations to gather real-world data on a technology. The developer is responsible for the cost of operating the equipment during the demonstration, while EPA is responsible for the analytical costs and evaluation associated with the demonstration. In most cases, the demonstration is performed at an actual Superfund site that provides appropriate site and waste characteristics for the specific technology to be tested.

CF Systems Inc., of Waltham, Massachusetts, developer of a liquified propane extraction technology, was selected to demonstrate their pilot-scale system. New Bedford Harbor was chosen for the demonstration of CF Systems' technology because the harbor sediments are contaminated with polychlorinated biphenyls (PCBs), a complex organic substance amenable to extraction with CF Systems' process.

The developer's pilot-scale treatment technology is a trailer mounted unit designed to handle pumpable soils, sludge, or sediments. The system was designed to be operated in a continuous, counter current mode. The unit operates in the six basic steps shown in Figure 1, that can cover extraction, phase separations, and solvent recovery. A mixture of liquified propane and butane was used as the extraction solvent.

The six process steps are: 1) pumpable (slurried) solid waste is fed into the top of an extractor; 2) the solvent, in this case a propane/butane mix, is condensed by compression and allowed to flow upward through the same extractor. In the extractor the solvent makes nonreactive contact with the waste, dissolving out the organics it contains. This is a somewhat nonspecific organic extraction process, though it is based on the solubility of the organic waste in extracting liquified gas; 3) the residual mixture of clean water or water/solids can be removed from the base of the extractor; 4) the mixture of solvent gas and organics leaves the top of the extractor and passes to a separator through a valve which partially reduces pressure--the reduction of pressure causes the solvent to vaporize out of the top of the separator; 5) extraction gas is then collected and recycled through the compressor as fresh solvent; and 6) the organics left behind are drawn off from the separator.

The demonstration was designed to evaluate the treatability of New Bedford Harbor sediments and to provide operating and scale-up data to assess potential commercial-scale applications. The demonstration included equipment setup; a "shakedown" stage to set process conditions; and daily start-up, operation, and shutdown. When tests were completed, the demonstration concluded with equipment decontamination and site closure. Thus, all of the major components of a full-scale cleanup.of New Bedford Harbor were demonstrated.

PURPOSE

Criteria were established to provide a basis for evaluating the pilot-scale unit. These criteria addressed treatment claims and operational claims made by the developer. Health and safety issues were also addressed throughout the demonstration. Data were collected during 4 tests for comparison against treatment and operational criteria and for assessing health and safety issues. The PCB concentrations contained in harbor sediments fed to the unit and the number of passes through the unit were varied for each of the tests.

Treatment Claims

CF Systems' treatment claim was to remove PCB contaminants from harbor sediments over the course of 4 tests. Test 1 was a shakedown test only. The feed rate and solvent to feed ratio were set and operating conditions were observed. Test 2 was conducted to show that harbor sediments with 350 ppm of PCB could be reduced by at least 90 percent after 10 passes through the unit. A pass was defined as one cycle, wherein treated sediment would be recycled through the unit. In Test 3, a 50 percent reduction was claimed after 3 passes for a 288 ppm sediment. Test 4 consisted of reducing a high concentration sediment, 2,575 ppm, to the Test 2 feed level, 350 ppm.

Operational Claims

System operating criteria were set during the shakedown portion of the demonstration. These criteria are shown in Table 1.

Extractor pressure was controlled at the unit's main compressor and at the organics discharge from the extraction segment of the unit. Solvent flow rate and the solvent to feed ratio are set after laboratory bench-scale tests were run on various mixtures of solvent and feed.

The feed temperature represents the temperature of the material pumped into the feed unit. Feed in the extractor was maintained above 60°F to avoid the possibility of hydrate formation, which could have interfered with the extraction process. If the feed is above 120°F, it must be cooled to prevent vaporization of the solvent.

The feed flowrate represents the rate at which material is pumped from the feed kettle into the unit. Operational flow rates above the listed maximum can force segments of the system such as decanters and control valves, beyond their effective hydraulic capacity.

The viscosity and solids content must be such that the feed material is pumpable. Feeds with a viscosity above the listed range were slurried with water to yield a pumpable viscosity. In order to prevent damage to the process equipment, the pilot-scale unit has a maximum limit for solids size.

Health and Safety Issues

Criteria were not established to evaluate health and safety issues; however, the health hazards associated with project activities were evaluated. The principal chemical hazards of concern for this project included polychlorinated biphenyls (PCBs) and toxic metals, including cadmium, chromium, copper, and lead. These chemicals were known to be present in contaminated harbor sediments. It was also suspected that some levels of gaseous propane, other organic vapors, and hydrogen sulfide would be encountered.

Volatilization of PCBs to harmful airborne vapor levels and/or increased airborne particulate concentrations, containing PCBs during initial sampling and feedstream preparation operations, were not considered to be likely because of the low vapor pressures of the PCBs and the wet characteristics of the sediment material. However, because of the toxicity of the PCBs, monitoring, repiratory protection, and complete dermal protection were required when handling contaminated sediments.

Air sampling and personnel monitoring were conducted to emulate chemical releases to the atmosphere. Soil samples were taken before and after the demonstration to determine if spills or atmospheric release had contaminated soils in the area where tests were staged. Finally, a carbon adsorption cannister mounted on the unit vent was analyzed to determine the amount of PCBs contained in propane vented from the unit during system shutdown.

APPROACH

Treatment Claims

Sampling and analysis were conducted for Tests 2, 3, and 4 to evaluate treatment claims. Test results are shown in Table 2. Samples were taken of (1) the sediments initially fed to the unit for each test, (2) sediments treated after each pass, or cycle, through the unit, and (3) extracted organics collected at the end of each test.

The critical analytical method was that used for the measurement of PCBs, since analytical data generated by this project would be used to evaluate quantifiably the developer's claims of PCB removal by the demonstration technology. EPA Method 8080 was used throughout the demonstration project to analyze PCBs. Other analyses were process control observations, and/or ultimate disposal determinations of project residues.

A detailed sampling and analysis plan and an approved Quality Assurance Project Plan (QAPP) were developed in accordance with EPA Office of Research and Development guidelines. The following analyses were conducted:

- PCB (soils, water)
- PCB (Soils)
- Waste Dilution
- Semivolatiles
- Trace Metals
- Particle Size
- Total Recoverable Oil and Grease
- Percent Solids
- EP Toxicity (metals)
- pH in Calcareous and Noncalcareous Soils
- Total Metals

Operational Claims

Process controls, wastestream masses, and utilities were measured at various intervals during each test. Listed below are critical operational parameters and measurement frequencies for each test:

- Feed temperature, viscosity, and pH--measured at each pass
- Feed sediment and treated sediment mass--measured at each pass
- Feed flow rate--measured every 10 minutes
- Extractor pressure and temperature--measured every 10 minutes

- Solvent flowrate--measured every 10 minutes

- Extracted organics mass--measured each test

The accuracy of devices used to measure pressure, temperature, flow, viscosity, and weight was below 5 percent relative standard deviation.

Health and Safety Issues

Several types of portable monitoring equipment were used during the tests, including:

- Portable Organic Vapor Analyzer (Century® OVA)

- Portable Photoionization Meter (HNu®)

- Combustible gas/oxygen/hydrogen sulfide meters (MSA® and Enmet-Tritector®)

- Detector tubes (Sensidyne-Gastec®)

- Personal air sampling pumps (Dupont-P200®).

The OVA and HNu® meters were used to monitor for organic vapors at all work stations on the unit, while personnel monitored process equipment. The OVA also was used as a survey meter on the process equipment to search for possible fugitive emissions from the equipment. Two portable combustible gas meters were used to check for elevated levels of propane and hydrogen sulfide during the equipment shakedown period and for spot testing during the demonstration. The pilot unit also contained two integral combustible gas detectors located on either end of the unit, which were observed during the tests.

Personal sampling was conducted using personal sampling pumps and 150-mg charcoal tubes and Florisil® tubes to determine personal exposures to organic vapors and PCBs, respectively.

Soil samples were taken from 10 locations in the test staging area to determine PCB levels in the soil prior to the demonstration. Samples of soil were taken at zero to six inches of depth. The 10 locations were resampled after CF Systems removed their equipment from the site and debris was removed from the site. The unit's carbon cannister was removed and sampled at the end of the demonstration after low pressure propane had been vented from the unit through the cannister.

At the conclusion of the tests, toluene was run through the unit to decontaminate unit hardware. Toluene was introduced to the unit as a feed material and system effluents were sampled and analyzed for PCB.

PROBLEMS ENCOUNTERED

The appropriateness of EPA Method 8080 for analysis of PCBs was questioned by several reviewers. It was believed that the extraction technology could selectively remove higher or lower molecular weight PCBs congeners. This possible selective extraction would not be apparent through use of Method 8080. The use of EPA Method 680 for PCB analysis was suggested by the reviewers.

Therefore, both methods were used during Test 4 and results were compared before the decision was made to use Method 8080 for all samples collected. Method 8080 is an analysis method for determining PCBs as Aroclors®. Analytical results reported for Aroclors® reflect an aggregation of individual PCB compounds, or congeners. With Method 680, each of the 209 PCB congeners is analyzed and reported as an individual compound. Analytical results obtained with Method 680 showed that any selective extraction that may occur would not be significant. The lower molecular weight PCBs were extracted with a 97 percent efficiency while the higher weight PCBs were extracted with 93 percent efficiency. Consequently, Method 8080, a lower cost method, was selected.

The duration of the test program was extended because of operational difficulties experienced with the sampling and analysis effort. Foaming occurred in the treated sediment collection tank which hindered sample collection. The unit irregularly accumulated and discharged feed material solids which prevented calculation of a PCB mass balance on a pass-by-pass basis. Finally, the lack of onsite PCB analytical capabilities did not allow field personnel to make quick adjustments to the process operations or sampling procedures. These types of problems were anticipated since the unit was designed for continuous operation but was operated in a batch mode during this demonstration. The developer believes that each of these sampling issues can be accommodated in the design and operation of a full-scale commercial system.

RESULTS

Treatment Claims

PCB concentration percentage reductions of PCB and reduction goals were as follows:

Test	PCB Concentration Reduction (%)	Reduction Goal (%)
2	89	90
3	72	50
4	92	86

Treatment claims were met for Tests 3 and 4. The treatment claim for Test 2 was not met after the tenth pass, however, a 98 percent concentration reduction was achieved by the ninth pass. It is believed that solids retained in the unit cross-contaminated treated solids discharged at the tenth pass which caused the tenth pass concentration to be higher than the ninth pass. EPA is using this information to identify the types of hazardous waste cleanup situations where the technology could be economically applied.

The performance of the treatment unit was evaluated in terms of extraction efficiency and a mass balance. Extraction efficiency per mass is defined as the input PCB concentration minus the output PCB concentration divided by the input PCB concentration (multiplied by 100 percent). Table 2 shows the extraction efficiency per pass for each of the three tests. Extraction efficiencies greater than 60 percent occurred at the first pass of each test. However, efficiencies ranged from zero to 84 percent in later passes. This wide range is probably due to solids retention, since changes in extraction efficiency did not correlate with changes in operating conditions.

Table 2 also shows solids output from the unit as a percent of the solids fed to the unit per pass. The data show that solids were irregularly retained and discharged by the unit. This was probably due to the small volumes that were batch-fed to the unit during each pass. Ordinarily, the unit would be run continuously over an eight hour working shift. However, schedule limitations only allowed run times of several hours per day. The nominal flow rate is 720 gallons per shift. During this demonstration, only 50 to 100 gallons were run per shift. Overall, a total of 794 pounds of solids were processed over 19 passes in Tests 2, 3, and 4. Of the total, 93 percent of the total solids were accounted for in effluent streams.

Even though solids retention caused cross-contamination of treated sediments, significant PCB removals occurred. For example, Test 2, Pass 9 contained 8 ppm of PCB. Compared with Test 2 feed (350 ppm), this represents an extraction efficiency of 98 percent. System decontamination procedures showed that PCBs were separated from the sediment since nearly all, 91 percent, of the PCBs were contained in extract subsystem hardware. Of the 81 grams of PCB fed to the unit during Tests 2, 3, and 4, only 4 grams remained in the final treated sediments. This indicates an overall removal efficiency of 95 percent.

Operational Claims

The unit generally operated within the specifications listed in Table 1 with only several exceptions. Criteria were met for feed flowrates, solids content, maximum possible size, viscosity, and pH as well as extractor pressures. The solvent flow rate and solvent to feed mass ratios fluctuated above and below criteria throughout the tests but did not have an observable affect on pass-by-pass extraction efficiency. Temperature of the feed sediments fell below the minimum temperature criterion during passes 6, 7, 8, 9, and 10 of Test 2.

Commercial-scale designs for application of the technology should ensure that operating specifications are maintained. Feed materials are likely to be well below 60°F throughout winter months and this could affect system performance. Therefore, heat must be added to sediments fed to a commercial-scale unit. Coarse solids removal will be required to maintain feed sediment paricle sizes below one-eighth inch. Wide fluctuations in the feed to solvent ratio should be minimized. Extraction efficiency is directly related to the amount of solvent available for solubilizing organics contained in the feed.

Health and Safety Issues

The Health and Safety Plan established procedures and policies to protect workers and the public from potential hazards during the demonstration. Implementation of these procedures and health and safety monitoring showed that OSHA level B protection is necessary for personnel that handle system input and output. Although, only OSHA level C protection is necessary for unit operators.

Combustible gas meters indicated that levels at approximately 20 percent of the lower explosive limit for propane were encountered while samples were taken. Background air sampling and personnel monitoring results indicate that organic vapors and PCB levels were present at levels below the detection limit for the analytical methods. Site soil samples taken before and after the demonstration indicate that demonstration activities did not result in increased PCB levels in the staging area soils. Therefore, no site contamination occurred due to the demonstration.

ACKNOWLEDGEMENTS

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FIGURE 1. SIMPLIFIED FLOW CHART

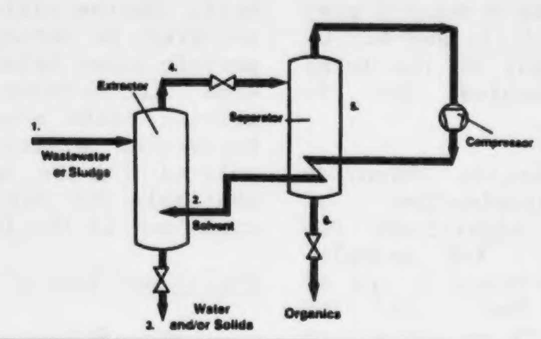

TABLE 1. OPERATING SPECIFICATIONS

	Minimum	Nominal	Maximum
Extractor Pressure (PSIG)	180	240	300
Extractor Temp. (°F)	60	100-110	120
Feed Temp. (°F)	60	70	100
Solvent Flow (pounds/minute)	8	12	15
Feed Flowrate (gallons per minute)	0.2	0.2-0.5	1.5
Solvent/Feed Ratio	1	1.5	2
Feed Solids (percent by weight)	10	30	60
Solids Size	--	—	1/8 inch
pH	6	7	12
Viscosity (centipoise)	0.5	10	1,000

TABLE 2. TEST RESULTS

Test Number	Pass Number	PCB Concentration (ppm)	Pass-by-Pass Concentration Reduction Efficiency (percent)	Solids Output As a Percent Of Input
2	Feed	350	Not Applicable	Not Applicable
2	1	77	78	60
2	2	52	32	90
2	3	20	62	135
2	4	66	No Reduction	45
2	5	59	11	125
2	6	41	31	90
2	7	36	12	100
2	8	29	19	150
2	9	8	72	110
2	10	40	No Reduction	110
3	Feed	288	Not Applicable	Not Applicable
3	1	47	84	115
3	2	72	No Reduction	90
3	3	82	No Reduction	85
4	Feed	2575	Not Applicable	Not Applicable
4	1	1000	61	80
4	2	990	1	130
4	3	670	32	80
4	4	325	52	90
4	5	240	26	75
4	6	200	17	135

Disclaimer

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ANALYSIS OF VAPOR EXTRACTION DATA FROM APPLICATIONS IN EUROPE

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ABSTRACT

Vapor extraction, an in-situ process to remove volatile organic compounds (VOC) from soils of the vadose zone, has been applied in Europe since the early 1980s. With considerably more than 1,000 systems operating under virtually all subsoil conditions, vapor extraction is considered to be a standard procedure in Germany.

In a vapor extraction well a negative differential pressure is created by a blower or similar device. The differential pressure generates a steady flow of soil gas towards the extraction well and thus provides a flushing of the soil with air undersaturated in respect to the contaminant concentration. Contaminants will evaporate into the gaseous phase both from the liquid phase and from the soil. Differential pressures applied range from 15" - 350" of water. The contaminated discharge air can be treated by activated carbon or other suitable methods. The effective radius of vapor extraction systems (VES) ranges typically from 20' to 150' underneath non-sealed - and up to 300' underneath sealed surfaces.

Parameters that influence the performance of the VES are the type of soil, depth to the groundwater, length of the screened section in the well, position of the screen, permeability of the ground surface and the type of blower used.

Discharge data from several hundred cases reveal typical common characteristics, regardless of the type of soil, type of blower and specific performance characteristics. Contaminant discharge is high during a first phase of about two weeks. A short second phase is marked by a transition to a stable level at around 10% of the initial concentration. In a third phase of several months to about two years the contamination decreases to background levels.

INTRODUCTION

Contamination from volatile organic compounds (VOC) have turned out to be widespread due to their almost ubiquitous presence in industrial processes. Specifically, VOC include halogenated hydrocarbons like TCE, PCE or TCA, aromatic hydrocarbons like benzene, toluene, xylene and volatile fuels like gasoline. Especially halogenated hydrocarbons exhibit physical properties that enable them to penetrate even coated concrete pads and seep into the ground rapidly, both as liquids and vapors. Significant contamination not only occurs at underground storage tanks, but also in drum storage, handling and application areas and along pipelines or transport paths.

Traditionally, soils that were contaminated with VOC were excavated and disposed of at a proper hazardous waste site. Due to the enormous amounts of waste generated and only limited storage capacity at the available disposal sites, the remediation is usually costly and only moves the problem-VOC contaminated soils - to another location.

Recognizing the problem, regulatory agencies increasingly favor on site and in situ remediation of soil and groundwater contamination. In addition, future regulations could further limit the availability of hazardous waste disposal sites and are likely to increase the already high costs of disposal. In the case of VOC contaminations, vapor extraction has shown to be an effective and economically feasible in situ remediation (3).

The high specific retention capacity of the vadose zone for VOC represents a continuous source of groundwater contamination, as even after a complete volatilization of the liquid phase material, vapors will continue to migrate. Remediation of the unsaturated zone by vapor extraction interrupts this migration path and is cost effective, since it captures the contaminants prior to dissolution in the groundwater (3).

Since vapor extraction is a widespread and generally accepted technology in Europe, particularly in Germany, the present paper draws on the experience gained by HARRESS Geotechnik since the early 80's through operation of roughly one thousand vapor extraction systems in Germany and throughout Europe and summarizes the results.

PURPOSE

The comparison of case histories and evaluation of vapor extraction serves several purposes. It
- outlines parameters, which determine the effectiveness of vapor extraction.
- shows the common discharge characteristics of vapor extraction systems in different geologic

settings and varying concentrations of contaminants.
- allows predictions on the development and progress of the remediation
- allows for design of a treatment system for the extracted vapors
- demonstrates that the technology has progressed from an experimental stage into a proven and reliable remedial process.

APPROACH

Six case histories have been selected for demonstration. The specific cases were chosen on the basis of their documentation, variety of settings, difference in contaminant concentration, type of contaminant, and optimum results of vapor extraction. The justification for selecting cases on the basis of the ideal performance of vapor extraction lies in the intention of this paper to show the predictability of the clean-up process, if all relevant parameters for the remediation are adequately considered. Knowledge of what to expect in the ideal case allows for detection of deviations which can point to a deficiency in the design of the system.

For comparison purposes, all discharge contaminant concentration data from the different vapor extraction systems were compiled in one graph. Integrations of the graphs were performed to estimate the volumetric balance during the remediation, i.e. percent of total contaminant discharge per unit time.

PROBLEMS ENCOUNTERED

The cited case histories represent the ideal progression of a remediation by vapor extraction. However, numerous sources for a deviation from the ideal pathway exist, leading to either an extended remediation or in the worst case to a failure to clean up the contamination. The two most common problems for clean up of the vadose zone are the placement of the vapor extraction system outside or at the periphery of the contamination center and a continuous recharge of contaminants into the subsurface. A continuous input can result from ongoing leakage/spills or from evaporation of VOCs from considerably contaminated groundwater. Misplacement of vapor extraction wells can be avoided by carefully defining the extent and the center of a source area.

A precise source definition is most efficiently done with soil gas investigations, the results of which also supply an appropriate basis for the calculation of projected contaminant concentrations in the discharge air.

Given this information, a vapor extraction system might still operate inefficiently if, in the presence of a very shallow groundwater table, vertical extraction wells with short screens are used. In such cases, a horizontal screen installation provides an effective solution.

RESULTS

Case Histories

Data from 6 case histories were compiled into a composite graph (Fig.1) and summarized on Table 1. In each of the case histories, vapor extraction has performed exceedingly well, either having already achieved a clean up or progressing in a way that a clean up can be predicted within the near future.

The curves appear to reflect three phases merging into each other. In all cases, the discharge concentrations decreased by 80% - 90% within the first 20 days of operation. After a steep decline lasting for 4 - 7 days (Phase 1), a less pronounced transisiton phase (Phase 2) is observed for another 10 - 12 days, eventually continuing in a gradual asymptotic decrease to background concentrations for the remainder of the operation (Phase 3). The initial phase is more pronounced if the discharge starts out at high concentration levels. During the long lasting third phase, it is conspiciuous that in five of the six case histories, the absolute concentrations vary within a comparatively narrow range. This is even more expressed if mass flow rates are regarded.

The progression of the decline of contaminant concentrations with time seems to be independent of the particular type of soil, initial concentrations or the specific characteristics of the vapor extraction system and well applied in each particular case.

In most cases, the measured data can be approximated by two regression curves. One of the curves fits the steep branch of the empirical contaminant concentrations curve, the second regression curve approximates the asymptotic decline in contaminant concentrations. While the regression curves do not allow a precise prediction of the time required for a complete clean up, they can serve as a guideline to monitor the progress of the remediation.

The distinct concentration decrease during Phases 1 and 2 could feign an equally rapid removal of contaminants from vadose zone soils. However, mass balance calculations illustrate the considerable contribution of the long-term operation at low concentrations. While 50% of the total amount of removable contaminants are discharged after a time period ranging from 1.5 weeks to 4 months, the removal of the remaining 50% is only achieved within 63 days to as many as 570 days of operation. In the cases presented, the total clean-up time ranged from more than 100 days to approximately 2.5 years.

FIGURE 1

VAPOR EXTRACTION

Discharge Performance

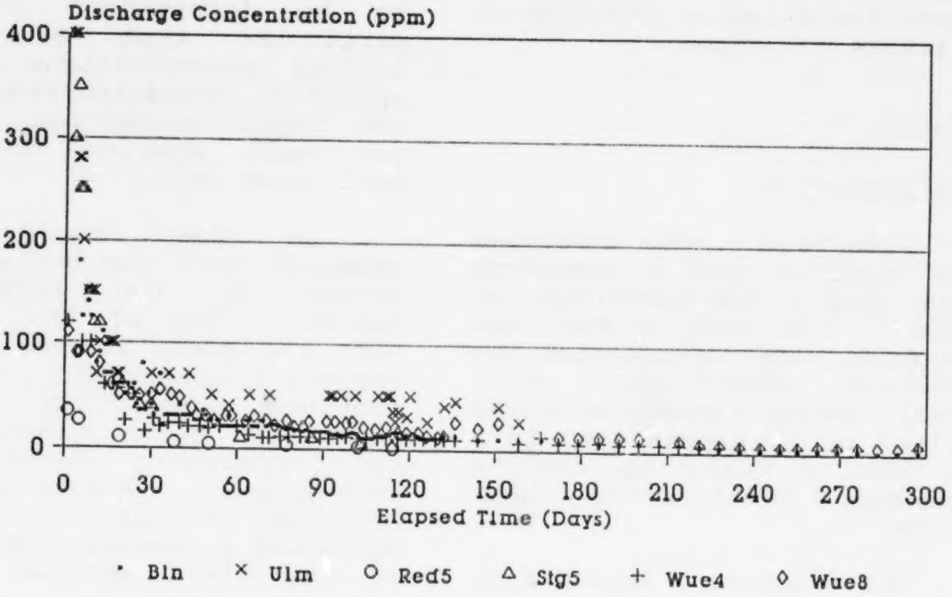

TABLE 1
CASE HISTORY DATA

	BERLIN (BLN)	WÜRZBURG (WUE4)	WÜRZBURG (WUE8)	REDWITZ (RED5)	STUTTGART (STG5)	ULM (ULM)
SOIL:	medium & fine grained sands	clayey silts w/limestone fragments	clayey silts w/limestone fragments	sandy-clayey silts	weathered claystone, silt	coarse grained fill, silty sands
CONTAMINANT:	PCE	PCE	PCE	PCE	TCE	PCE
VOLUME FLOW:	390 CFM	68 CFM	70 CFM	50 CFM	75 CFM	103 CFM
RANGE OF INFLUENCE:	180′	40′	40′	60′	50′	75′

Physical Processes in the Soil

Unless a continuous recharge of contaminants at high rates is encountered, the presence of free product in soils is typically limited to small fluid particles trapped in soil pores (4). At the expense of these fluid droplets as well as of compounds dissolved in the soil moisture or adsorbed to the soil matrix, a contaminant vapor phase will develop and spread over time controlled by the concentration gradient.

After an initial exchange of the soil gas volume in the pores, ambient air will be drawn continuously from outside the contaminated area. While passing through the subsurface the air will be charged with evaporating VOC and subsequently be discharged through the vapor extraction system (1). The process resembles a continuous flushing of the soil with clean air and will continue until volatilization and desorption of contaminants is complete.

The three phases describing the system performance are attributable to different processes occuring during the operating time. During the first phase the contaminant saturated soil gas, which is present in the pore space under equilibrium conditions, is discharged. A rapid evaporation of free product droplets due to disturbance of the equilibrium is presumably also in part occurring during the first phase. The short transitional period, when the contaminant concentration in the discharged soil gas has already decreased by more than 80%, is most likely characterized by a shift in source of the contaminants. Rather than from an evaporation of liquid particles, the contaminants in the discharge vapors result from a desorption of contaminants from soil particles. A second process, which is believed to become important in this phase, is the transition of contaminants previously dissolved in the soil moisture into the gaseous phase (3).

The third phase represents the comparatively slow desorption process and a gradual reduction of the contaminated soil volume. The time this period requires depends on the physical properties of the compounds involved and the mass of VOC retained in the soil. As long as sufficient supplies of contaminants are existing, a nearly constant extraction rate is accomplished over a period of several months up to about two years.

Data from air flow models indicate a rapid decrease of pressure differentials to very low levels with increasing distances from the vapor extraction well (2). The differential pressures throughout the majority of the range of influence are too low to be directly responsible for enhanced volatilization of the contaminants. However, even very small differential pressures create a pressure gradient and thus induce the flow of air towards the vapor extraction well. The equilibrium disturbance caused by this process, rather than enhanced volatilization through large differential pressures is considered to be responsible for the extraction of contaminants.

Design Parameters

Aside from the type of soil, the range of influence of a vapor extraction system is determined by a number of factors, in particular by the length and position of the screened interval in the extraction well, the thickness of the vadose zone, and the permeability of the surface. Differential pressures decrease exponentially with increasing distance from the extraction well. While higher differential pressures create considerably higher volume flow rates, the effects on the range of influence are small. For example, in medium grained sands an increase of the differential pressure raises the volume flow exponentially, while the effective radius remains almost unaffected (2).

Given a constant differential pressure, variations of the screen length reveal a linear relationship between the length and the volume flow rate, and also a distinct increase of the effective radius. The position of the screened interval creates reciprocal effects: shifting it to deeper portions of the vadose zone reduces the volume flow but increases the range of influence (2).

Under the assumption of a screened interval of constant length positioned in the middle portion of the vadose zone, an increasing thickness of the vadose zone results in a distinct increase of the range of influence, while it seems to have only minor effects on the volume flow (2).

The same effect can be observed if variably sized areas of surface sealing are regarded. The presence of an impermeable layer, such as a concrete pad, gives rise to significantly increased ranges of influence at almost constant volume flow rates. However, a sealed surface is not a prerequisite for the successful application of vapor extraction systems.

Aside from theoretical model calculations, the actual range of influence of single systems or arrays should be determined in the field. This can be done in several ways, ways, by actually repeatedly measuring the soil gas concentrations at varying distances by measuring the differential pressure created in air monitoring points, or just by qualitatively determining the existence of a differential pressure through the observation of smoke trails created by air current tubes at such points.

SUMMARY

In order to achieve a successful remediation of the vadose zone by vapor extraction, a continued input of contaminants into the subsurface, evaporation of contaminants from a plume of contaminated groundwater and positioning of the vapor extraction well outside the contamination center must be ruled out. A thorough assessment of the contamination pattern is, thus, a prerequisite.

To properly address the problem, various system design parameters are to be considered. They include the length and position of the screened well interval(s), as well as the selection of the appropriate suction device.

The application of the results of previous experiences with vapor extraction as exemplified in the case histories allow:

- a prediction of the development of contaminant concentrations in the discharge air with time.
- design of a treatment system for the discharged vapors
- timely recognition of factors impeding or preventing a successful clean up by comparing the actual curve with the projected ideal curve.
- optimized design of vapor extraction wells.

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Disclaimer

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IN-SITU BIOREMEDIATION OF CYANIDE

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ABSTRACT

So that manufacturing operations would not be interrupted, in-situ bioremediation was chosen for soil remediation after a release of cyanide beneath the main floor of an electronics manufacturing facility. Laboratory studies were conducted to (1) determine the effectiveness of stimulating naturally occurring bacteria to effect bioremediation of cyanide and (2) determine optimum nutrient conditions for the bioremediation system. Seven equal fractions of a basic medium containing 2,400 ppm cyanide were placed into capped reactor tanks; carbon and phosphate concentrations were adjusted differently for each tank. Cyanide was removed at a very rapid rate in all of the tanks. While the tanks varied in their initial and final rates of cyanide removal, all achieved similar overall rates. Engineering design for construction and operation of nutrient mixing and feed systems and for groundwater extraction are presented.

INTRODUCTION

An active electronics manufacturing facility experienced a subsurface release of zinc cyanide plating solution from an underground storage tank located beneath the main floor of the facility. The tank excavation was limited, to avoid damage to the building structure. Although removal of the tank was accomplished, contaminated soil and shallow groundwater remained. Soil cyanide concentrations were on the order of 15,000 ppm at the excavation walls, decreasing to less than 100 ppm within about 25 feet of the excavation area. Remediation was complicated by the need to restore the floor area so that production operations could resume. A remediation approach was needed which would be as unobtrusive as possible.

This paper presents the results of laboratory studies conducted to evaluate the effectiveness of in-situ bioremediation of the remaining cyanide. The technical approach focused on stimulation of naturally occurring bacteria. Optimum nutrient conditions were determined. The engineering approaches for construction and operation of nutrient mixing and feed systems and for groundwater extraction are also presented.

BIOCHEMISTRY

Although generated by some plants, many fungi, and a few bacteria, cyanide is toxic to most organisms. Cyanide is a specific inhibitor of porphyrin-type biochemical systems. These include iron-containing cytochromes and hemes associated with respiration, oxygen transport, and electron transport. Also sensitive to cyanide are the plastcyanins (copper-containing proteins associated with photosynthesis) and cobalt porphyrins such as vitamin B-12.

Some microorganisms, however, are very tolerant of or resistant to cyanide. Bacillus pumilus is reported to tolerate 0.1M potassium cyanide.

Although ammonia is readily assimilated and is the preferred nitrogen source for almost all microbes, some bacteria can use cyanide compounds as a nitrogen source. Cyanide metabolism can serve the dual purpose of supplying nitrogen and detoxifying cyanide. The organisms responsible for cyanide degradation are generally alkaliphilic.

The simplest systems for microbial use of cyanide as a nitrogen source utilize cyanide hydratase and cyanide oxygenase. The hydratase system generates formamide and formate with the release of ammonia. The multicomponent oxygenase system forms carbon dioxide and ammonia.

Alternative mechanisms for cyanide-nitrogen assimilation are the synthesis of thiocyanate and its subsequent oxidation to carbon dioxide and ammonia, and of cyanoalanine, which may be converted to asparagine and aspartic acid. Generation of thiocyano-aminobutyrate is apparently a dead-end detoxification process.

Not surprisingly, microbes rarely use cyanide as a carbon source. Carbon dioxide, the usual carbon product of cyanide degradation, is energetically expensive to assimilate. With the exception of autotrophic bacteria, as well as scavenging pathways, the vast majority of microbes prefer or are obligated to use organic carbon sources for the vast bulk of their carbon.

APPROACH

Soil borings were advanced from the surface of the tank excavation and near the expected boundary of the contaminated zone to determine the extent of contamination and to provide soil samples for characterization of biological activity and laboratory treatability studies. Monitor wells were installed near the expected boundary of the contaminated zone to help determine the extent of contamination.

To determine treatability, seven capped reactor tanks were established as identically as possible. The basic medium for all the reactors was mixed and sampled as one batch before the additions of phosphate and a carbon source. Cyanide levels were 2,400 ppm (about 0.1M). Seven equal fractions of the basic medium were individually adjusted for their phosphate and carbon source concentrations. Phosphate concentrations were adjusted according to the schedule shown in Table 1.

A 1:1 molasses/Karo syrup (high fructose) mixture was used as the carbon source. Aldose sugars are known to be excellent carbon sources for cyanide degradation due to a stabilizing interaction with the cyanide and an ability to act as an excellent aerobic energy source. The concentrations of the mixtures in the

Table 1. Concentrations of Compounds in Reactor Tanks (ppm)

Compound	Tank Number						
	1	2	3	4	5	6	7
Cyanide	2,400	2,400	2,400	2,400	2,400	2,400	2,400
Phosphate	0	100	100	100	1,000	100	10
Molasses/ Karo Syrup 1:1	100	0	1,000	10	100	100	100

tanks were adjusted according to the schedule shown in Table 1. The tanks were capped gas tight and sampled on days 0, 4, 7, 11, 14, 21, 28, 32, and 35. The samples were assayed for ammonia, cyanide, colony-forming units (CFU; using typticase soy agar (TSA) plates), and toxicity (Microtox™).

RESULTS

Cyanide concentrations decreased in every tank (Figure 1). There were slight differences in time course, but cyanide in all tanks decreased to about the same level within 35 days. In every tank, cyanide removal plateaued between days 11 and 21. This plateau was associated with ammonia accumulation (Figure 2), which may have had a toxic effect on cyanide removal. An alternative and perhaps more likely possibility is that both ammonia and cyanide were responding to a common effector and not to each other. Oxygen depletion in the closed system may have limited the removal of cyanide and the generation of ammonia.

Ammonia levels declined in all tanks after day 21, the day the tanks were opened to the air. The tanks remained open for the duration of the study. Cyanide removal was excellent during the active periods. The removal rate for the days 0 to 11, averaged for all tanks, was 5.03 mg/kg/hr (ppm/hr) (Table 2).

The marginally best overall treatments were in Tanks 1, 2, and 3. Cyanide removal rates for treatments 1 and 2, days 21 to 32, were the highest, although all tanks were slower during days 21 to 32 than they were during days 0 to 11. While the

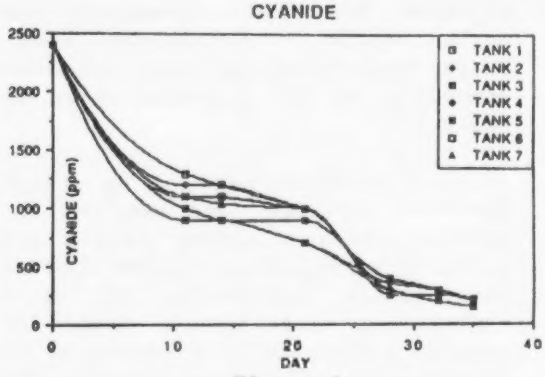


Figure 1

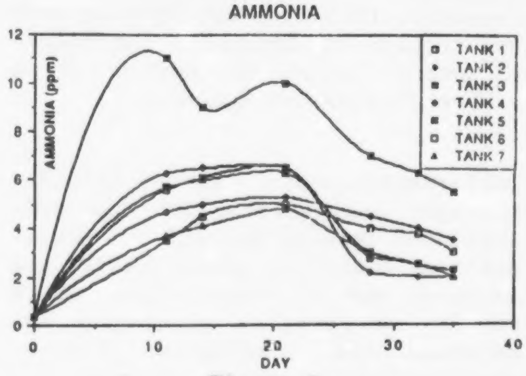


Figure 2

Table 2. Cyanide Removal Rates (mg/kg/hr)

Tank Number	Time Period (days)			
	0 - 11	11 - 21	21 - 32	0 - 32
1	4.17	1.25	3.03	2.86
2	4.55	0.83	3.03	2.86
3	5.68	0.83	1.89	2.86
4	5.68	0.83	1.52	2.73
5	5.30	0.42	2.27	2.73
6	4.92	0.42	2.80	2.79
7	4.92	0.42	2.80	2.79
Average	5.03	0.71	2.48	2.80

tanks varied in their initial and final rates of cyanide removal, all achieved similar overall rates. Tanks with faster rates between days 0 and 11 were slower between days 21 and 32.

Figure 3 illustrates the close correspondence of ammonia generation and cyanide removal ,rates in all of the tanks. The cyanide concentration appeared to be controlling the overall removal rates, suggesting that the removal of cyanide was enzymatic. Faster removal earlier gave lower cyanide concentrations later. Those lower concentrations then caused a slower enzymatic removal rate later. There was little difference between the seven tanks. The stripping of cyanide observed in other investigations would not seem to be a mechanism for cyanide removal in these experiments because the system was closed during the initial period of active removal.

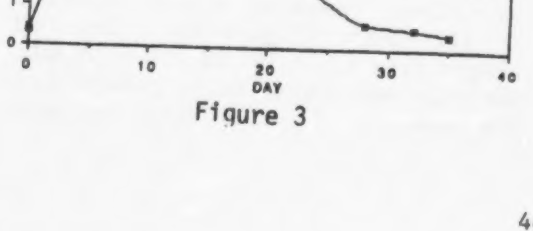
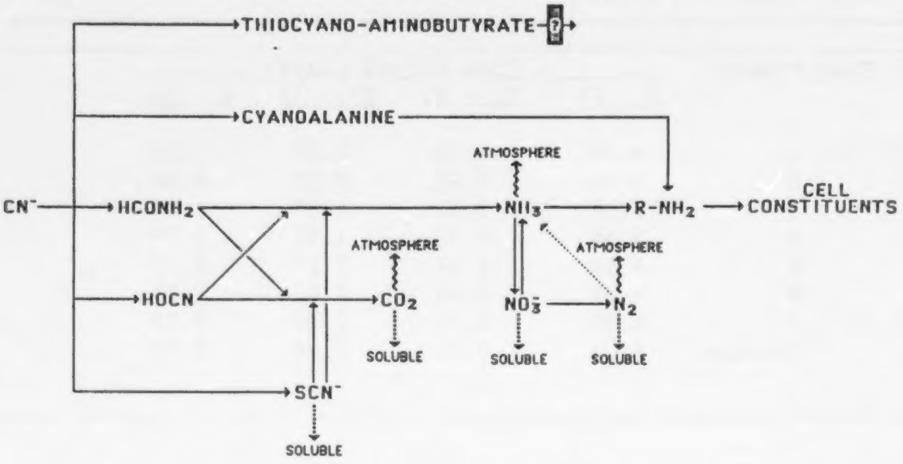


Figure 3

Cyanide disappeared at a very rapid rate in all of the tanks. Simple mass balance calculations indicated that not all of the cyanide removal was accounted for by the ammonia measured in the tank liquors. There are several reasonable explanations for this effect, none of which diminishes the excellent removal rates for cyanide. As Figure 4 indicates, there are several possible fates for ammonia generated from cyanide. The most likely explanation is that, for any of a multitude of possible reasons, the CFU data do not reflect actual cell populations. The counts suggest that no growth in cell populations has occurred, which seems unlikely. If the cell populations actually increased from 1.5-2.0 x 10^4 to approximately 1.5-2.0 x 10^7 cells, a very modest increase for a microbial population, then the unaccounted-for ammonia could be explained as cell constituents. A less likely explanation is that ammonia was formed, mineralized to nitrate/nitrite with the oxygen present,



POSSIBLE FATES OF CYANIDE

Figure 4

and then denitrified to dinitrogen when the oxygen was exhausted. This appears unlikely because of low oxygen availability during the initial days of the experiment.

Ammonia was generated as cyanide was removed (Figure 3), suggesting that the ammonia was generated from the cyanide. But, as mentioned above, the total ammonia produced does not account for the cyanide lost in the tanks. If the tank having the highest level of ammonia were kept closed, the ammonia generated by day 32 would only account for approximately 1% to 2% of the cyanide removed (Tank 5). Since the CFU data remained constant, unaccounted-for nitrogen was not in cell constituents unless CFU data does not reflect actual cell populations.

Removal of the caps on the tanks lowered ammonia, presumably through loss to the atmosphere. A conclusion that ammonia was inhibiting cyanide removal could be drawn since the decrease in ammonia concentrations was followed by increased cyanide removal. An alternative explanation, as mentioned above, is that both systems are dependent on cell metabolism. When oxygen is depleted, the metabolism stops. When the metabolism stops, ammonia and cyanide metabolism stop. Opening the tanks allowed oxygen to enter. Oxygen reinitiated the ammonia generation and cyanide removal. Because of the open tanks, ammonia accumulation was no longer detected at increasing levels, while cyanide was removed as before.

Tank 5 accumulated the most ammonia, and was also the only tank with 1,000 ppm phosphate added. This indicated an apparent relationship between high phosphate availability and ammonia accumulation, which may have been a function of the increased buffering capacity of phosphate. There was not a similarly clear relationship between cyanide removal and phosphate. The high ammonia accumulation in Tank 5 was seen at every time point (Figure 5).

Microbial plate counts (demonstrated by CFU/ml) remained almost constant in all tanks (Figure 6). The CFU ranged from 1.4×10^4 to 2.0×10^4/mL. Not only was there little growth, but the numbers of cells detected were

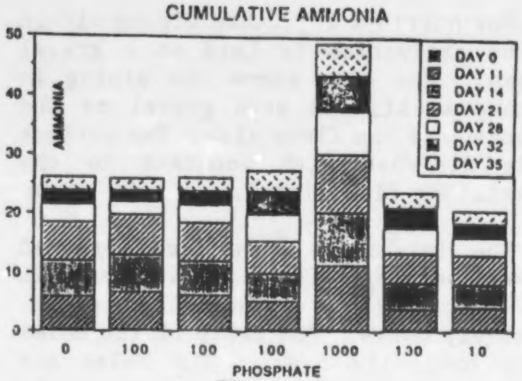


Figure 5

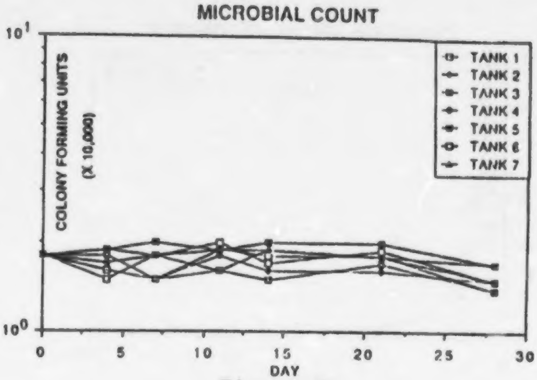


Figure 6

very low in all the tanks. Soils may have 10^6 to 10^8 cells/g even in deep subsoil. The results suggest that either the enumeration medium was not detecting all of the organisms present or that cyanide had a sterilizing/inhibitory effect. An approximation of the organism-to-cyanide ratios suggests that over the 35-day period each microorganism would have to had degraded billions of molecules of cyanide per minute. This seems unlikely and supports the idea that the cell-counting medium failed to enumerate all of the viable organisms, or that a nonenzymatic process was removing the cyanide.

The relative toxicities of the tank liquors were assayed by the Microtox™ technique. The toxicities in all tanks remained constant and high until the opening of the tanks at day 21 (Figure 7). Toxicities did not decline, whereas the cyanide concentrations declined from 2,400 ppm to approximately 900 ppm in each tank. When the tanks were opened and cyanide levels fell below 400 ppm, the relative toxicities decreased dramatically. The relationship between this decline in cyanide concentration and decrease in toxicity is approximately logarithmic (Figure 8).

SYSTEM INSTALLATION

Based on the results of the laboratory testing presented herein, a field bioremediation system was installed at the subject facility. This installation coincided with the removal of the plating solution tank and utilized the tank excavation as part of the bioremediation system. The field bioremediation system consists of three main elements: (1) nutrient injection system, (2) nutrient supply system, and (3) groundwater gradient control system. A cross-section of the field bioremediation system is shown in Figure 9.

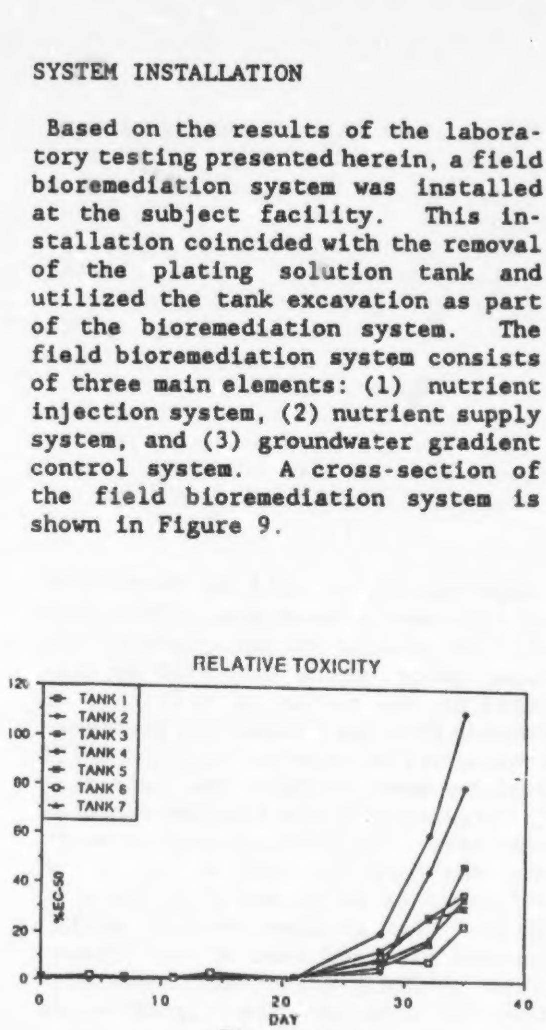


Figure 7

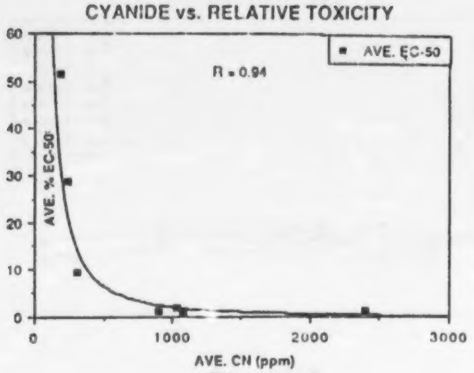


Figure 8

The nutrient injection design incorporates slotted piping laid on a gravel bed in the excavation and a series of injection (well screen) points located around the perimeter of the excavation. Both slotted piping and injection points are connected to a nutrient supply system that will be used to supply nutrients to the subsurface. Injection pressures are expected to vary from 2 to 5 psi. Changes in pressure (injection rate) are due to subsurface soil heterogeneity and rates of saturation.

Injected fluids will be introduced into the unsaturated zone. The fluids will be allowed to percolate to the water table, where they will be captured in the radius of influence of pumping from the extraction/gradient-control wells. Gradient-control wells will be used to limit the potential for migrating fluids from the remediation area. The gradient-control wells are designed to have a radius of influence of 60 ft and a drawdown of 20 ft. Two gradient-control wells, located east and west of the excavation, should provide sufficient control to preclude the migration of water away from the remediation zone.

The nutrient injection piping within the excavation is laid on a gravel bed. The area above the piping is then backfilled with gravel to the bottom of the floor slab. The surface is finished with concrete to the existing floor level.

The injection points are screened well points (1-ft sections) placed in sand-backfilled predrilled (4-in. auger) holes. The depth of the holes is nominally 5 ft. The holes are grouted with neat cement above the screened interval well points. There are approximately 20 well points spaced at 10-ft centers arranged near the perimeter of the remediation area. All well points are connected by a header system to the constant head nutrient supply system.

Bacterial growth is expected to occur predominantly around the perimeter, and to gradually move toward the most contaminated zone at the edge of the excavation.

CONCLUSION

Cyanide is readily and rapidly removed in the tested system. While the disappearance of cyanide does not parallel the formation of ammonia or the development of biomass, there is no doubt that cyanide is being dramatically removed. The disappearance of cyanide also is not linearly paralleled by decreased toxicity. Cyanide in all tanks decreased to below 900 ppm before toxicity consistently decreased. The decrease is logarithmic in relation to cyanide concentrations. This effect is probably explainable as a threshold value or "window" of toxicity. The evidence indicates that bioremediation is a rapid and effective means of removing cyanide from contaminated soils and subsoils in situ, particularly when the proper nutrient and oxygenation conditions are maintained.

The system is scheduled for startup of nutrient injection during the summer of 1989. Ongoing analytical testing will be performed during the remediation effort to substantiate the in-situ biological removal of cyanide, to supplement data collected during laboratory testing, and to monitor the progress of the in-situ bioremediation.

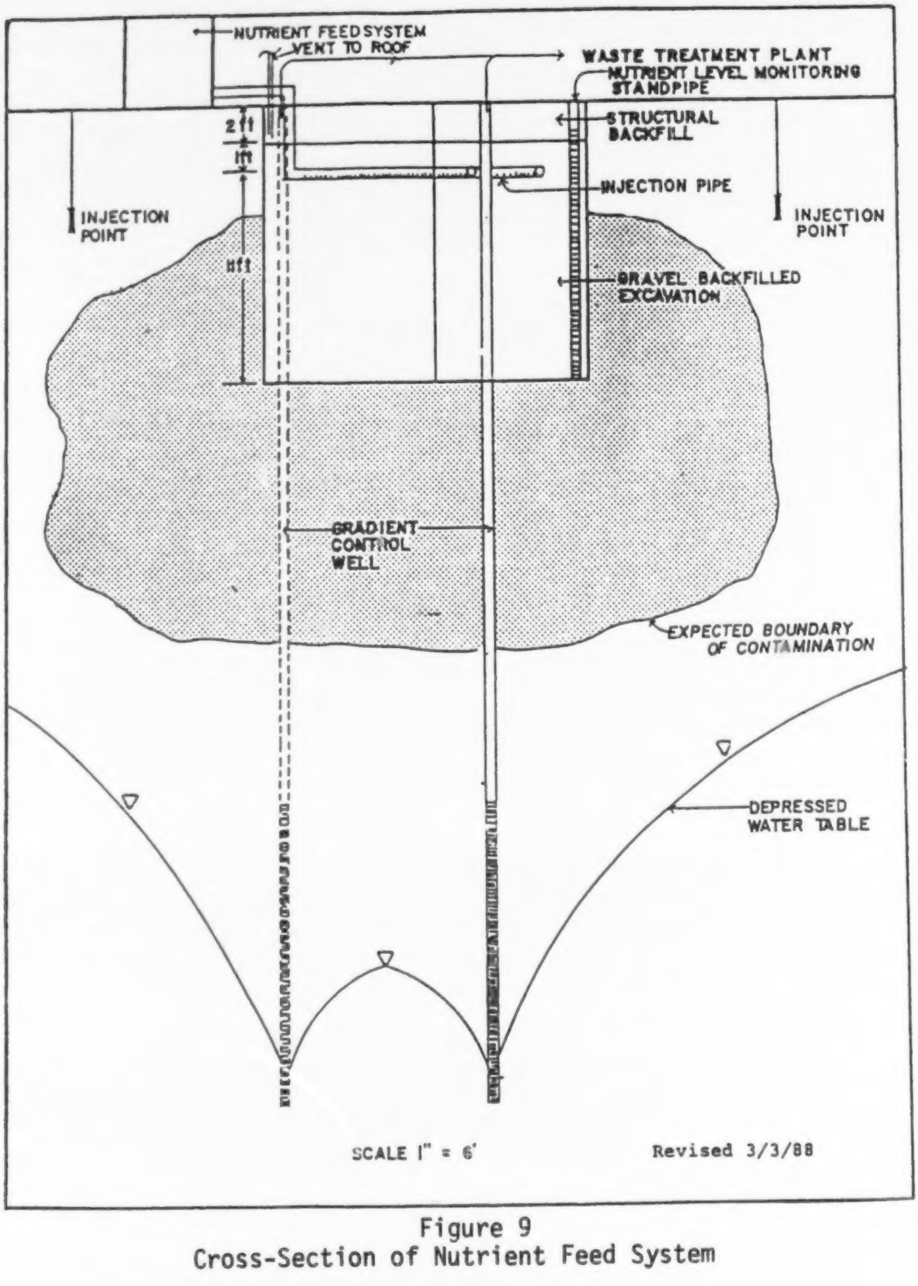

NUTRIENT FEED SYSTEM
VENT TO ROOF
WASTE TREATMENT PLANT
NUTRIENT LEVEL MONITORING STANDPIPE
2 ft
1 ft
STRUCTURAL BACKFILL
INJECTION PIPE
INJECTION POINT
INJECTION POINT
11 ft
GRAVEL BACKFILLED EXCAVATION
GRADIENT CONTROL WELL
EXPECTED BOUNDARY OF CONTAMINATION
DEPRESSED WATER TABLE
SCALE 1" = 6'
Revised 3/3/88

Figure 9
Cross-Section of Nutrient Feed System

Disclaimer

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EVALUATION OF ALTERNATIVES FOR IMPOUNDED HIGH SALT WASTES CONTAMINATED WITH ORGANIC AND INORGANIC POLLUTANTS

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A waste impoundment with a flexible membrane liner (FML) was suspected of contributing to subsurface contamination and the Denver area client contracted with IT for a technical and economic evaluation of alternatives for stopping this potential source.

The sludge and brine contents of the pond included wastes from the chemical milling of aluminum, other heavy metals, organics, fluoride, nitrate and high concentrations of other dissolved salts.

IT first conducted a paper evaluation of alternatives to identify those that were readily implementable and cost effective. Eight technologies were screened, using engineering judgement and assumed performance to prepare preliminary estimates of efficiency and cost. On and off–site disposal of residuals were considered. Three technologies were selected for additional investigation – direct solidification, solar evaporation, and a combination of solid/liquid separation and steam evaporation.

Bench and pilot–scale treatability tests were then performed to experimentally measure key performance and cost parameters. Solar evaporation was simulated in an innovative lab system. The data were then used to refine the performance and cost estimates for the client.

INTRODUCTION

The waste impoundment was used as an evaporation pond for the myriad of wastes resulting from chemical milling of aluminum, surface preparation of other metals, and various metal working, plating and finishing operations. The waste in the pond is comprised of a predominant sludge layer and a small overlying aqueous layer; the total volume was estimated to be 1 million gallons (5000 tons). The types and concentration ranges of the contaminants in this impoundment are summarized in Table 1.

As expected, an impoundment used for this purpose contains high levels of heavy metals, total dissolved solids (TDS), nitrates, fluorides, and organics. A large amount of aluminum is present in the sludge. Identified volatile organic compounds were <2 ppm, and semi–volatiles (chiefly phenols and polynuclear aromatic hydrocarbons) were approximately 10 ppm. Based on TOC content there is a large amount of unknown organics of low water solubility. This material is classified as hazardous based on EPA classifications F001 to F005, pH, and chemical composition.

The client was located on a pristine mountain stream that flowed to the city's drinking water reservoir, so treatment requirements for discharge of any treated water were very stringent.

PURPOSE

IT Corporation contracted to provide the client with an identification and evaluation of alternative technologies for ending this potential source of subsurface contamination at their site. The results of this evaluation were a recommendation of the cost effective treatment and disposal technology for closure of the impoundment.

The objective of this project was to identify and evaluate those options that are environmentally sound, minimize long–term liability, minimize the amount of material to be shipped off–site and are cost effective.

APPROACH

A two–phase approach was used to carry out this project. Phase I was a paper study to screen alternatives on assumed technical performance and preliminary cost comparisons. Phase II was to conduct bench and pilot–scale testing of the three alternatives identified in Phase I to generate experimental data on performance and to refine the cost estimates of Phase I.

Factors which were considered in screening technologies were:
- technical performance
- simplicity of operation
- availability of equipment, preferably mobile and for lease
- minimal technological risk
- ease of scale–up
- air emissions potential
- cost
- feedback from client

Two basic disposal options for each of the closure alternatives were identified:
- on–site disposal of the treated pond inventory in either the existing pond area or a solid waste landfill after delisting, or
- off–site disposal at either a hazardous waste landfill or at a solid waste landfill after delisting.

In other words, the pond inventory could be handled as a hazardous waste or treated to delisting criteria and be handled as a solid waste.

Three basic approaches to dealing with the evaporation pond contents were identified, and various treatment schemes within each were conceptualized. The three approaches were:
- Solidification of the entire waste by addition of chemical additives to convert sludge and aqueous to a solid mass that would pass the paint filter test or the TCLP test.
- Separation of water from chemicals; because of the high inorganic content, technologies common to brine concentration and processing were identified.
- Separation of chemicals from water; this is the traditional approach to processing aqueous wastes, whereby a series of unit operations are used to remove or react the various organic and inorganic contaminants, producing a purified water for discharge.

Within these categories, several technologies were screened based on IT experience and either accepted for more detailed consideration or rejected.

The three technologies identified for further evaluation in Phase I were direct solidification, solar sludge drying beds, and a treatment combination of solid–liquid separation, evaporation, and solidification of solids.

For the Phase II experimental testing, a composite sample of the pond contents was collected and shipped to IT's Technology Development Laboratory in Knoxville, Tennessee. Bench and pilot scale test results were used to prepare technical and economic comparisons of the three technologies identified in Phase I.

PROBLEMS ENCOUNTERED

The only significant problem was how to simulate solar sludge drying beds in the laboratory. In solar sludge drying, the incident radiant energy of the sun is used to supply the heat required to evaporate water in the sludge. Preliminary estimates in Phase I had indicated that it might take six months to evaporate the sludge sufficient to pass the paint filter test.

IT designed a bench–scale experimental system that used a sun lamp positioned above a covered bed of sludge. Incident energy from the lamp at various positions on the sludge surface was determined using a pyranometer. The data collected were used to calculate the size of a covered drying bed and the length of drying time under solar conditions in the Denver area.

RESULTS

Fourteen technologies were screened on a preliminary basis and either accepted or rejected for further evaluation.

Eight alternatives were selected for more detailed assessment of technical and cost factors in Phase I.

1. Direct solidification of the entire pond contents with cementitious additives.

2. Evaporation with sludge drying beds under a translucent cover.

3. Evaporation by direct flame injection of slurry in a sonic pulse jet dryer.

4. Evaporation in a horizontal, heated dryer with agitation, additional heating, and forward movement of the solids provided by a hollow screw through which steam is circulated.

5. Sludge separation into solids, water, and organics with the B.E.S.T. solvent extraction process.

6. Solid/Liquid Separation by a mobile filtration or centrifuge system.

7. Evaporation to treat the aqueous phase from the solid/liquid separation step to separate organics, dissolved solids, nitrates, and fluorides from the water.

8. Treatment of evaporated water condensate.

The alternatives recommended for further testing and evaluation in Phase II were:

1. Direct solidification of evaporation pond sludge and liquid to either a) pass the paint filter test for land disposal as a hazardous waste at an approved off–site facility or in an on–site vault or b) to fixate sludge and hazardous constituents for possible de–listing and landfill disposal.

2. Drying of the sludge in an evaporative drying bed, covered but open to the atmosphere; disposal of the dry solids as is or after stabilization.

3. Treatment via solid/liquid separation, evaporation of separated liquid, condensation and treatment of evaporator condensate, and solidification of all solids produced.

These alternatives are shown schematically in Figures 1, 2, and 3.

1. Direct Solidification Test Results – Fly ashes and cement kiln dusts local to the Denver area were used to solidify the composite sample to two degrees: to pass the PFT and stabilized to pass the TCLP test. Bench scale testing showed that 0.1 tons of fly ash or 0.2 tons of cement kiln dust per ton of sludge were sufficient to pass the PFT. For stabilization the required amounts were 1.0 tons of fly ash or 0.75 tons of cement kiln dust per ton of sludge, and volume expansion was 67%, and unconfined compressive strength ranged from 3–5 tons per ft^2. The samples passed the TCLP test.

2. Solar Sludge Drying Beds – Calculations showed that the rate limiting step for solar sludge drying was the transfer of the heat required to evaporate the water. The volume of air and its relative humidity were not rate limiting factors. To prevent rainwater from falling onto the sludge during drying, an elevated plastic cover made of materials designed to transmit most of the sun's energy is placed over the drying beds. The covered area is open on the sides to allow free air movement over the sludge.

The experimental laboratory testing set–up consisted of a polyethylene tray to hold the sludge placed in an insulated enclosure covered with a piece of Sunglo 17 CL reinforced, colorless fabric covering furnished by the Covertec Corporation of Birmingham, AL. Its solar transmittance is 87%. The tray was filled to a depth of approximately 3 1/4" with 5.3 kg of sludge. The drying chamber was purged with air at a rate well below the 8.5 mph average wind velocity in Denver. Humidity, temperature, and hydrocarbons in the air purge were monitored.

Solar energy was simulated by irradiating the surface of the sludge with a 375 watt infrared lamp with a silvered internal reflector. Adjustment of lamp power output was by a variable power transformer. The lamp was positioned above the center of the tray at a distance of 0.5 meters. The energy imparted to the sludge through the cover at different lamp power settings was measured using a direct measuring pyranometer. Readings were taken at the center and at the four corners in the tray. Actual energy transparency to the wavelength ranges measured by the pyranometer was found to be in the range of 60–65%. These data were used to calculate the energy input to the surface of the sludge during drying.

Drying with heat (lamp on) was done periodically to simulate alternating day and night periods. The sludge surface was irradiated for 8 hours per day for 10 days; the total drying time was 218 hours. The air purge was uninterrupted for the total time. During that time the water content of the sludge was reduced from 80% to approximately 20%.

The sludge was mixed by hand using a rake–type implement twice per day, at the beginning and end of the light period. The weight loss of the sludge in the tray was measured daily.

The air purge humidity ranged from 20–40% and its temperature ranged from 65 to 96 F. The hydrocarbons in the purge air were measured using a GC/FID instrument and ranged from 2 to 14.9 ppm (average 5 ppm) during the first 100 hrs, then dropped to 1–2 ppm during the next 40 hrs. Also, no odors were detected.

Using the sun lamp calibration data, the hours of irradiation, and the daily water evaporation, the energy which was necessary to evaporate one pound of water per day from the sludge was calculated. The average for days 1 through 8 was 2967 BTU/lb water. These sludge drying daily energy results are shown in the graph shown in Figure 4. The changes in the slope of the drying curve readily shows the loss of free water, steady state drying, and a sharp rise in slope during final drying.

For a sludge drying period of six months in the Denver area, the total solar radiation incident at the surface were obtained from USGS data. Daily solar energy ranges from 310 Langleys (gram–calories/cm2) in October to 525 Langleys in June. Total Langleys for the May–October period are 81,249. Converted to BTUs/ft^2 it is 299,000. Correcting for the 87% transmittance rating of the cover, only 260,000 BTU/ft^2 are available.

To evaporate 1,000,000 gal of sludge @ 80% water to 40% water, the energy required is 1.98 x 1010 BTU. This translates to a sludge bed drying area of 1.75 acres. An area of 2 acres makes an allowance for downtime and other inefficiencies. This would produce 1670 tons of dried solids from 5000 tons of sludge.

The dried solids from the sludge drying tests, which were at 20% moisture, were re–hydrated to 40% water. This additional moisture was added to provide water for hydration of the cement kiln dust used for stabilization. Stabilizing with 3.75% kiln dust and 4% lime yielded a product that passed the TCLP test.

3. Sludge Dewatering/Evapor–ation/Solidification – Bench and pilot–scale tests were used to characterize the performance of this treatment sequence (see Figure 3) in separating chemicals from water.

Batch sludge dewatering tests were run in a pilot belt filter press (BFP) and a bench–scale vertical solid bowl centrifuge. The BFP gave the highest solids content, 43%; anionic flocculant at 650 ppm was found to produce the best dewatering characteristics. These BFP data translated to a production rate of 17 gal/min on a 2 meter wide press, a relatively low filter press rate.

Filtrate from the pilot BFP tests and centrate from the bench centrifuge tests was combined and batch evaporated in a glass bench–scale test unit. Heat was supplied by an electric heating mantle. Vaporized water was condensed and analyzed for TOC, then subjected to bench–scale tests of carbon adsorption, gas stripping, and chemical oxidation to further reduce TOC in the condensate.

Evaporation of 94% of the volume of the aqueous feed produced a condensate that ranged from 15–20 ppm TOC. The 6% bottoms product was a salt slurry that contained 64%

solids. No scaling of the glass heat transfer surfaces was noted.

Treatment of the condensate with activated carbon in IT's micro–column adsorption test apparatus produced no removal of TOC. Purging of the condensate with nitrogen reduced TOC by ≈ 10 ppm. Further treatment of the stripped condensate with hydrogen peroxide and bleach produced no reduction of TOC.

The wet cake from the BFP tests and the salt slurry from the evaporator were combined in a 10/1 ratio and solidified with 75% cement kiln dust. This level of additive is equivalent to 0.48 tons per ton of original pond sludge. This stabilized sample passed the TCLP test.

SUMMARY

For the three alternatives evaluated in Phase II, the summary of the quantities of treated pond waste for disposal are presented in Table 2.

For off–site disposal of residuals from these three alternatives, transportation and placement in a hazardous waste landfill in Utah was the lowest cost. The combined transportation and disposal cost was $260/ton.

A summary of the estimated treatment cost for each of the alternatives is presented in Table 3. It shows the costs for on–site disposal and off–site disposal, stabilized to either pass the PFT or the TCLP.

The recommended approach to closure of this pond was direct solidification of the entire pond contents with sufficient fly ash or cement kiln dust to pass the TCLP and have sufficient strength to support installation of a temporary cap.

Table 1. Evaporation Pond Sludge Data:General Physical/Chemical Parameters

Parameter	Concentration Range	Mean
pH	10.0 – 10.4	10.2
% Water	73 – 85%	79%
Total Organic Carbon	6,600–14,000 mg/kg	11,000 mg/kg
Chemical Oxygen Demand	2,400–24,000 mg/kg	10,000 mg/kg
% metals (35 metals analyzed)	29 – 33%	31% (dry weight)
Anions		
Nitrogen as Nitrate	11,000–22,000 mg/kg	14,000 mg/kg
Fluoride	11,000–36,000 mg/kg	21,000 mg/kg
Cyanide	4.8 – 54 mg/kg	30 mg/kg
Phosphorus as Phosphate	2,500–4,600 mg/kg	3,900 mg/kg

Table 2. Summary of Quantities for Disposal, tons

Alternative	Solidified to Pass PFT	Stabilized to Pass TCLP
1. Direct Solidification	5,500–6,000	10,000–8,750
2. Solar Drying Beds	1,670	1,800
3. Solid/Liquid Separation, Etc.	3,190	5,575

Table 3. Summary of Estimated Costs (all dollars in thousands)

	On–Site Disposal	Off–Site Disposal		
	Treatment	Treatment	Disposal	Total Treatment Cost
Alternate 1				
Pass PFT	118	118	1,430	1,548
Pass TCLP	265	303	2,275	2,578
Alternate 2				
Pass PFT	1,262	1,253	434	1,687
Pass TCLP	1,300	1,291	468	1,759
Alternate 3				
Pass PFT	742	675	829	1,504
Pass TCLP	929	862	1,450	2,312

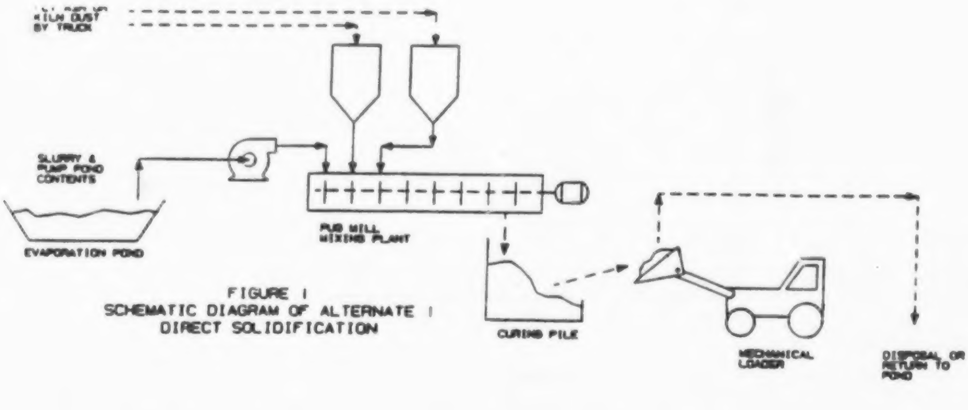

KILN DUST
BY TRUCK
SLURRY &
PUMP POND
CONTENTS
EVAPORATION POND
PUG MILL
MIXING PLANT
CURING PILE
MECHANICAL
LOADER
DISPOSAL OR
RETURN TO
POND

FIGURE 1
SCHEMATIC DIAGRAM OF ALTERNATE 1
DIRECT SOLIDIFICATION

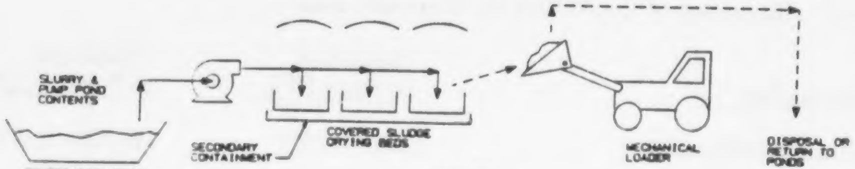
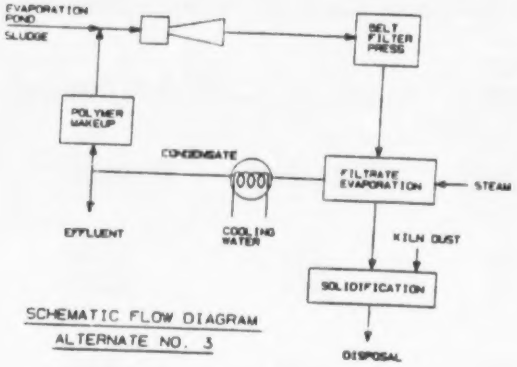

SLURRY & PUMP POND CONTENTS
EVAPORATION POND
SECONDARY CONTAINMENT
COVERED SLUDGE DRYING BEDS
MECHANICAL LOADER
DISPOSAL OR RETURN TO PONDS

FIGURE 2
SCHEMATIC DIAGRAM OF ALTERNATE 2
SLUDGE DRYING BEDS


EVAPORATION POND
SLUDGE
BELT FILTER PRESS
POLYMER MAKEUP
CONDENSATE
FILTRATE EVAPORATION
STEAM
EFFLUENT
COOLING WATER
KILN DUST
SOLIDIFICATION
DISPOSAL

SCHEMATIC FLOW DIAGRAM
ALTERNATE NO. 3

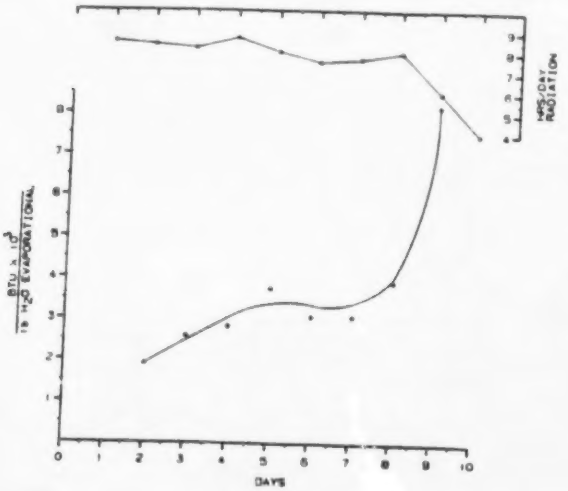


FIGURE 4
SLUDGE DRYING SUMMARY

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

KPEG Application From The Laboratory To Guam

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ABSTRACT

The novel reagent generically named APEG (alkaline polyethylene glycolate) can be very effective for dehalogenation of a variety of halo aromatic pollutants. The PCBs, PCDDs, PCDFs even PCTs (polychlorinated terphenyls) can be effectively dehalogenated by APEG reagents to yield non-toxic products. The reagent has been shown to be effective on these classes of pollutants in a variety of matrices from sediment to soils and waste oils.

Early work in 1986 with KPEG performed on PCDD and PCDF contaminated oil (9000 gal.) in Butte, Montana demonstrated the effectiveness of the KPEG system on these types of hazardous wastes. Early tests of the _in situ_ application of KPEG on dioxin contaminated soil in Missouri demonstrated some limitations of the reagents applicability. The most severe drawback for _in situ_ KPEG application is the reagents extreme hygroscopisity. These early experiences led to the design of the pilot-scale chemical reactor system for the effective use of the APEG reagent. This reactor system was first demonstrated on a heavily PCB-contaminated site in Guam, USA during April-May 1988. This pilot-scale unit was capable of treating from one to two tons of contaminated soil per batch. Further refinements were made to the reactor system after careful examination and analysis of the first eight reactor batches. During September-October of 1988 these refinements were employed in a second series of KPEG treatments in Guam. Contaminated soil containing from 500 to 2,600 ppm of PCB closely resembling Aroclor 1260 was treated with the KPEG reagent. The only residual PCB peak detected in the soil treatments was a tetrachlorobiphenyl, ranging from approximately 1 ppm to nondetectable levels. The KPEG reagent was also applied to treating all of the contaminated tyvek clothing, gloves and boots from the combined runs during the 1988 year. Sampling of the reactor contents revealed the presence of tetra-, penta-, and hexa- chlorobiphenyls but at below the one part per million range. These results demonstrate the capability of the KPEG reagent to perform chemical dehalogenation on haloaromatics in a variety of matricies, ranging from oils to soils and contaminated clothing.

INTRODUCTION

Compounds which have gained notoriety for their persistence as well as their toxicity are the halogenated aromatics. Most notable among this class or organics are the chlorinated dibenzodioxins (PCDDs) dibenzofurans (PCDFs) and the polychlorinated biphenyls (PCBs). In the last few years PCDDs and PCDF's have increasingly been identified in chemical product waste streams as well as effluents from incineration processes. The accumulation of PCDDs, PCDFs, PCBs and other toxic halogenated compounds in the environment and living systems is a serious problem that has been well documented. Although a great amount of work has been done by many groups in the area of direct chemical decomposition of halogenated organics, relatively little effort has been directed toward on-site chemical detoxification.

There are currently some chemical methods available to alter or decompose PCBs and other haloaromatics in contaminated oils. The methods developed by Acurex, Goodyear and Sun Ohio, involving dispersion of metalic sodium in oil or the use of sodium-biphenyl or naphthalene mixtures are commercially available. However, due to the reactivity of these sodium formulated reagents with water they present a serious draw back with their use on haloaromatic contaminated soils, sediments, sludges or dredgings. Other chemical reactions have been evaluated for dehalogenation of environmental pollutants but have not been found to be adaptable to field conditions. (1, 2, 3)

Up to this time one of the most reactive chemical dehalogenation systems for use in the aforementioned area of decontaminating soils has been the alkaline polyethylene glycolate moiety (APEG). The alkali most commonly used for this reagents preparation is potassium hydroxide (K), in conjunction with a polyethylene glycol ranging from molecular weight of 300 to 600 Daltons. This reagent, labeled KPEG, is tolerant of wet matrices in which it is to be used for dehalogenation of said haloaromatics eg. the PCBs PCDDs and PCDFs. Though the chemistry of APEGs can be traced back to the early 1970s it was not until the summer of 1978 that this reagent was demonstrated efficacious at dehalogenation of PCB in contaminated oils. (4) Since that time a series of APEG reagents have been prepared, which with heating produce rapid dehalogenation of haloaromatic compounds (5, 6, 7, 8). The basic reaction scheme for the dehalogenation of an haloaromatic is shown:

(1) HOPEG + KOH - KOPEG + H_2O (2)
Aryl-Cl+KOPEG - Aryl-O-PEG+KCl   (3)
Aryl-O-PEG - Aryl-OH+Vinyl-PEG

In equation (1) the appropriate polyethylene glycol is reacted with potassium hydroxide to form the reactive APEG species. This preparation step may be performed directly in the contaminated matrix which is to be treated. Reaction (2) takes place over a wide temperature range from ambient to ca 110°C. The third reaction (3) shows conversion of the ether linked PEG/Aryl moiety to a phenolic with consequent release of a vinyl terminal polycthylene glycol. This reaction generally takes place at temperatures above 110°C. In some of these reagent formulations dimethyl sulfoxide is added as a cosolvent to enhance reaction rate kinetics presumably by improving rates of extraction of the haloaromatic contaminant into the alkoxide phase. (7)

In 1982, detailed investigations were initiated to determine the effects of variable reaction parameters on the rate and extent of chemical decontamination of soils (9). This research focused almost exclusively on the direct chemical treatment of PCB contaminated soil. The first field investigation aimed at identifying treatment conditions for chemical destruction of PCDDs and PCDFs in oil recovered from the ground of a wood preserving site in Butte Montana was initiated in January of 1986. (10) In November of 1987 plans were made to perform a Pilot Scale Evaluation of the KPEG processes' effectiveness in treating PCB (Aroclor 1260) contaminated soil at the U.S. Navy's Public Works Center in Guam. Two separate Pilot Scale tests were performed, the first during March/April 1988 and the second during September/October 1988.

PURPOSE

During January 1986 research and field investigations were initiated to determine if a chemical reagent ie. the KPEG reagent, could be used to effectively treat PCDD and PCDF contaminated oil at an industrial wood preserving site near Butte Montana. The site contained approximately 9,000 gallons of a light petroleum oil collected previously from groundwater over a two year period. The oil contained, 3.5% pentachlorophenol and PCDD and PCDF homologs ranging from 422 part per billion (ppb) of tetra-isomers to 83,923 ppb octa-isomers. The process successfully decontaminated the petroleum oil during July 1986.

The PCB contamination at the U.S. Navy Public Works Center in Guam ranges from a few hundred ppm to well over 40,000 ppm of Aroclor 1260. This contamination resulting from the previous practice of emptying and draining transformer oil on to the very porous coral soil surrounding the transformer rebuilding shop. The contaminated area is of several acres in size. Due to the large expense of containerizing and shipping this soil from Guam to an approved incineration facility, the U.S. Navy decided to examine the potential for on-site decontamination of this soil utilizing the KPEG reagent.

APPROACH

Decontamination of PCDD and PCDF containing oil

In April 1986, U.S. EPA Region 8 agreed, after a review of laboratory data, that the KPEG process could be used to decontaminate the PCDD/PCDF tainted oil on-site. The site being a former wood treating facility located near Butte Montana.

The mobile field equipment employed to implement the previously mentioned chemical decontamination process comprised of a 2,700 gallon batch reactor mounted on a 45 foot trailer equipped with a boiler, cooing system and a laboratory/control room area. Heating of the raw oily waste/KPEG reagent mixture was achieved by the recirculation of the oil and reagent through a pump, a high shear mixer and a tube heat exchanger which was heated by a boiler or cooled through a series of fin-type air coolers. The process was successfully employed in July of 1986 to decontaminate some 9,000 gallons of this PCDD/PCDF tainted oil. The results are shown in Table 1.

Table 1. TREATMENT OF CONTAMINATED OIL, BUTTE, MONTANA

Contaminants CDD/CDF	Concentration in Untreated Oil (ppb)	Concentration in Treated residue (ppb) 70°C, 15 min.	100°C, 30 min.	*MDC
TCDD (2,3,7,8-)	28.2	-	-	0.65
TCDD (total)	422	-	-	0.37
PeCDD	822	-	-	0.71
HxCDD	2982	-	-	2.13
TCDF (2,3,7,8-)	23.1	12.1	-	0.28
TCDF (Total)	147	33.3	-	0.35
PeCDF	504	-	-	0.36
HxCDF	3918	4.91	-	0.76
HpCDF	5404	5.84	-	1.06
OCDF	6230	-	-	2.62

* Minimum detectable concentration in parts per billion (ppb)

Decontamination of Arolor 1260 Containing Soil

In November 1987 a 400 gallon Littleford reactor was purchased for use in demonstrating a Pilot scale application of the KPEG process on the Aroclor 1260 contaminated soil located in Guam. This reactor and all ancillary equipment required for its use were shipped via the Navy from Port Hueneme California to Guam in February 1988. During March 1988 the reactor was outfitted and provisions were made to employ the analytical instruments located at the Naval FENA laboratory on Guam for the PCB treatment analyses. The goal of this KPEG treatment of the PCB contaminated soil was to achieve a maximum residual concentration of no more than 2 parts per million (ppm) of any chlorobiphenyl isomer to remain in the soil.

Processing of PCB Contaminated Soil in Guam I

Typically from one to one and one half tons of contaminated soil were loaded into the reactor. This was followed by addition of 50% by weight of Polyethylene glycol average molecular weight 400 Daltons (PEG-400) and the appropriate quantity of potassium hydroxide (89% flake) to yield an equi molar ratio to the PEG-400. After the chemicals had been added to the reactor, the unit was sealed and heated to 140-150°C for 3-5 hours. Any distillate was captured and condensed, final venting was through a carbon trap. The results of this first series of KPEG treatments is in Table 2.

As these results show, there are greater than 2 ppm residual PCB congeners in batches 1, 6, 7 and 8. These therefore did not comply with the permit requirement of less than 2ppm per resolvable congener remaining after treatment as imposed by the U.S. EPA.

This resulted in a series laboratory scale KPEG reactions being performed in the U.S. EPA RREL Research Laboratory in Cincinnati. Here it was discovered that the increase of base, eg KOH over the equi molar ratio to PEG-400 of from 1:1 to 1.3 - 1.5 : 1 resulted in the

Table 2: Comparison of Guam soil prior to and after KPEG treatment.

Batch #	Aroclor in PPM Prior to Treatment	PPM of residual PCB Uncorrected	Corrected *
1	1,990	Tetra-Cl BP = 2.11 penta-Cl BP = 5.42 hexa-Cl BP = 7.33	= 2.24 = 6.46 = 6.50
2	1,740	tetra-Cl BP = 1.87	= 1.99
3	1,490	tetra-Cl BP = 1.36	= 1.45
4	1,540	tetra-Cl BP = 1.82	= 1.94
5	1,010	tetra-Cl BP = 1.80	= 1.91
6	1,140	tetra-Cl BP = 4.12	= 4.38
7	1,140	tetra-Cl BP = 3.27	= 3.38
8	1,860	tetra-Cl BP = 4.64	= 4.94

* Corrected values calculated by extraction efficiency of mono through deca chlorobiphenyls from this soil.

desired lowering of all the residual PCB congeners previously mentioned. This resulted in a return trip to Guam during September - October 1988 to demonstrate this improvement on the KPEG process.

Guam II

The treatment during this second phase of the pilot scale investigation consisted of loading the reactor with the same 50% weight of PEG-400 to soil but with an increase of 30% of KOH to PEG-400 over stoichiometric. As is demonstrated by the results in Table 3, Retreatment of Original Guam Soil, the PCB congeners which remain are reduced to below the 2 ppm limit. The efficacy of the improved KPEG process is further demonstrated by the results as shown in Table 4, Continuation of Guam Soil PCB Treatment, where all residual PCB congeners are either not detected or below the 2ppm limit.

As condensate was emitted in this treatment process, it had to meet emission standards as for the treated soil. The results of condensate analysis are shown in Table 5, Reactor Emission, Condensate Samples.

Table 3: Results of Retreatment of Original Guam Soil

Batch #	PPM OF RESIDUAL 1ST Run	PCB (corrected) RETREATMENT
1	TETRA-CL BP = 2.24 PENTA-CL BP = 6.46 HEXA-CL BP = 6.50	= 0.48 = ND = ND
6	TETRA-CL BP = 4.38	= 0.85
7	TETRA-CL BP = 3.48	= 0.15
8	TETRA-CL BP = 4.94	= 0.66

ND = NONE DETECTED

Table 4: Continuation of Guam Soil PCB Treatment

BATCH #	AROCLOR IN PPM PRIOR TO TREATMENT	PPM OF RESIDUAL PCB CORRECTED
9	919	TETRA-CL BP = 1.01
10	19 PPM *1	TETRA-CL BP = 0.22
11	298	ND
12	529	TETRA-CL BP = 0.59
13	*2	TETRA, PENTA, AND HEXA-CL BP ALL LESS THAN 1 PPM

ND = NONE DETECTED

*1 = MATERIAL RESIDING IN REACTOR AFTER VENT FAILURE CONSISTED OF PRIMARILY A PENTA AND HEXA CHLOROBIPHENYL.

*2 = THIS LOAD CONSISTED OF SHREDDED CONTAMINATED TYVEK CLOTHING, GLOVES AND BOOTS. THE ORIGINAL PCB CONCENTRATION WAS NOT DETERMINED.

Table 5: REACTOR EMISSIONS, CONDENSATE SAMPLES

BATCH #	PPM RESIDUAL PCB
1*[1]	ND
6*[1]	< 1 PPM
7*[1]	< 1 PPM
8*[1]	< 1 PPM
9	ND
10	< 1 PPM
11	< 1 PPM
12	< 1 PPM
13	*2

ND = NONE DETECTED

*1 = THESE ARE THE BATCHES WHICH WERE RETREATED.

*2 = NO CONDENSATE SUBMITTED FOR ANALYSIS.

PROBLEMS ENCOUNTERED

The treatment of PCDD/PCDF contaminated oil with the KPEG reagent was very efficacious. There were no problems encountered in scale-up of the laboratory procedure used in testing the KPEG reaction on samples of the contaminated oil.

The application of the KPEG process to PCB contaminated soil in Guam revealed a potential problem. This problem, namely residual PCB congeners being above 2 ppm in concentration in some of the treated batches of Guam contaminated soil was overcome. The retreatment of these aforementioned batches and successful treatment utilizing the improved KPEG treatment process was demonstrated.

This is not to say there were no other problems encountered in either of these treatment demonstrations. There were logistical problems, ie difficulties in having all equipment at all the required places at the time of use. However, as is demonstrated, these problems were also overcome.

RESULTS

As can be seen in Tables 1 thru 5 the treatment of both oil and soil contaminated with haloaromatics is feasible from a laboratory to pilot scale utilizing KPEG reagents. The reagent can successfully reduce PCDD/PCDF levels from thousands of parts per billion to non detectable levels in a contaminated oil matrix. Further the KPEG reagent can be used to reduce PCB levels resulting from Aroclor 1260 contamination in soil to less than 2 PPM, within a reasonable time frame.

This demonstrates the use of the KPEG Systems applicability to a variety of haloaromatic pollutants in a variety of matrices.

ACKNOWLEDGEMENTS

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

TESTING NATURAL ZEOLITES FOR USE IN REMEDIATING A SUPERFUND SITE

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ABSTRACT

The U.S. Environmental Protection Agency's (EPA's) Risk Reduction Engineering Laboratory (RREL) has recently completed a project to evaluate the effects of adding natural zeolites to a soil contaminated with metals. The objectives of this project were to: (1) determine the engineering properties (including hydraulic conductivity) of several amendment-soil combinations; and (2) identify those metal ions in the soils that could be sorbed, and therefore immobilized by the zeolites.

A screening program was performed to determine which of five commercial zeolite products were most effective in controlling metal ion mobility. The effectiveness of the five zeolites was evaluated using a simple batch leaching procedure: The Monofilled Waste Extraction Procedure (MWEP). The MWEP extracts were analyzed for several metal ions, including lead, chromium, and zinc, using ICP. This was done to determine which zeolite product retained the most metal ions following the MWEP procedure. The two zeolites which removed the most metals of interest from the MWEP solution were then used in a more detailed laboratory investigation.

The laboratory investigation involved several tests in addition to the MWEP. These were: (1) permeameter seepage tests to measure the effect of the zeolites on permeability, and (2) standard physical and engineering soils tests (e.g., moisture content, particle size distribution, Atterberg limits, specific gravity). The total test program also included the Bunker Hill Superfund site soil amended with agricultural limestone for comparison purposes. The results of the MWEP and permeameter seepage tests are discussed in this paper.

INTRODUCTION

The Region X Office of the U.S. Environmental Protection Agency (EPA) is responsible for the remediation of numerous Superfund sites in the northwestern United States where large quantities of soils have been contaminated with heavy metals. These metals can and have caused environmental and human health impacts. Environmental pathways for migration of metal contaminants include mobilization of metals present in soils by solubilization in groundwater and/or surface water, dispersion of metals with fugitive dusts, and uptake of metals present in soil by plants. Each of these pathways presents potential exposures to humans and wildlife. EPA Region X officials, who were aware of the ability of natural zeolites to preferentially sorb metals, requested that EPA's Risk Reduction Engineering Laboratory provide technical assistance in evaluating zeolites as soil amendments.

PURPOSE

The purpose of the work described herein was to: 1) select and evaluate the relative effectiveness of several commercial grades of the naturally occurring zeolite, clinoptilolite, in reducing metal concentrations in water extracts of amended Superfund soils; and 2) evaluate the effect of zeolite amendments on the leachability, and physical and engineering properties of amended Superfund soils.

LITERATURE SURVEY

More than 150 synthetic zeolites and 40 natural zeolites are known (2). Synthetic zeolites have enjoyed a wide range of applications, but to date they have been too expensive to be used in large-scale applications for remediation of hazardous waste sites. Until recently it was believed that natural zeolites were not abundant enough to be an economically feasible replacement; however, large deposits of zeolites discovered in the western United States make these minerals a viable alternative to synthetic zeolites. The most common types of zeolites (clinoptilolite, mordenite, chabazite, and erionite) originated by the natural alteration of volcanic ash in alkaline environments.

Some of the other applications in which natural zeolites are used for their ion exchange ability are in detergents, as water softeners, in ammonia/ammonium removal from fresh-water effluents, in radioisotope removal from spent nuclear reactor pile effluent, and in agriculture as a carrier of ammonium and potassium.

In addition to ion exchange, the uniform pore sizes of zeolites (ranging from 0.3 to 0.8 nm) can selectively adsorb or reject molecules or ions based on their size or shape; this is known as the molecular sieve effect. Another type of adsorption separates components based upon differences in their selectivities. Catalysis can also occur within the intracrystalline void.

Several researchers have found that clinoptilolite can be used to selectively remove heavy metal ions from water. Semmens and Seyfarth (8) conducted studies that showed that clinoptilolite samples, one treated with NH_4Cl and one washed with acid, exhibited very high selectivities for barium and lead and somewhat lower selectivities for copper, cadmium, and zinc in displacing sodium. The lead and zinc exchanges were not highly reversible. Semmens and Martin (7) looked at the removal of lead, silver, and cadmium by clinoptilolite in the presence of competing concentrations of calcium, magnesium, and sodium. The selectivity sequence was found to be $Pb^{2+}>Ag^{+}>Cd^{2+}$, with excellent removal of lead. Lead and cadmium removal decreased with the presence of competing cations in the order $Mg^{2+}>Na^{+}>Ca^{2+}$. Calcium concentrations significantly inhibited cadmium removal.

Studies have also been conducted on ammonium removal by natural zeolites (3). Blanchard, et.al (1) investigated the removal of ammonium and heavy metal ions from drinking water and found that the selectivity of the sodium-exchanged clinoptilolite decreases in the order $Pb^{2+}>NH_4^{+}>Cu^{2+}$, $Cd^{2+}>Zn^{2+}$, $Co^{2+}>Ni^{2+}>Hg^{2+}$. Loizidou and Townsend (5) found that lead was exchanged to a greater extent than cadmium, in the absence of competing cations, on sodium clinoptilolite. They calculated a "maximal level of exchange" (a ratio of mol/kg exchanged metal to mol/kg of total aluminum) of 0.795 for lead and 0.656 for cadmium.

Work has also been conducted on using zeolites as soil amendments, which are defined as substances that aid plant growth indirectly by improving the condition of the soil. Soil amendments should not be confused with plant nutrients, such as nitrogen, that are used directly by the plants. Natural zeolites have been used in Japan as soil amendments for years because of their ion exchange and water retention capabilities. Lai and Eberl (4) added NH_4^{+}-saturated clinoptilolite and phosphate rock to soil. Phosphate rock provides nutrients, but its use as a fertilizer is limited because of its low solubility. The zeolite serves as a sink for Ca^{2+} ions that exchange with the NH_4^{+} ions, thereby reducing the concentration of Ca^{2+} in solution and allowing more phosphate rock to dissolve. The ion exchange ability of zeolites may also be able to trap heavy metals in soil and prevent their uptake by plants. Nishita and Haug (6) conducted studies indicating that addition of clinoptilolite to soil contaminated with Sr^{90} decreased strontium uptake by plants.

APPROACH

The experimental approach involved determination of the relative ability of several zeolite treatments to reduce the concentrations of metals in water extracts of contaminated soils. In addition, the leachabilities of the amended soils were determined. The specific natural zeolites used, clinoptilolites, were obtained from three mines in eastern Oregon. Soils from two Superfund sites were initially included in a screening test program; however, only one soil was used in the full test program. This soil was obtained from the Bunker Hill Superfund site in Kellogg, Idaho. Lead, up to two percent by weight, was the major contaminant in this soil. The second soil, used in the screening test program only, was obtained form the United Chrome Products, Inc., (UCPI) Superfund site in Corvallis, Oregon. Chromium was the major contaminant in the UCPI soil. Both the zeolites and the test soils used in this evaluation were collected by EPA Region X personnel prior to commencement of the study.

A screening test of the relative efficacy of five natural zeolites as soil amendments for the two Superfund site soils was conducted. These five grades are mined near Adrian, Oregon, and were designated as CH-5, CH-20, XY-5, XY-20, and SC-35 by the mining company. The letter symbols differentiate the zeolites based on the type and location of the natural deposit and the quality characteristics of the mineral; and the numbers indicated the screen mesh size through which the commerical product passes. The relative efficacy was determined by comparison of dissolved metal concentrations in water extracts of amended soils and nonamended soils (i.e., controls). This was accomplished by mixing the zeolites, in six mix ratios, with the test soils and subjecting the amended soils to the Monofilled Waste Extraction Procedure (9). This procedure (MWEP) consists of four sequential extractions of sample using ASTM Type 2 deionized water in a liquid/solid ratio of 10:1. Based on these screening tests, two zeolites and one Superfund soil were prepared, as were nomamended control samples and samples amended with agricultural limestone. The limestone amendment was evaluated to allow comparison of test results with a standard agricultural practice. Additionally, the physical and engineering properties of the soils were determined.

RESULTS

MWEP Screening Test Program

The screening test program resulted in selection of CH-20 mesh and XY-5 mesh (from five clinoptilolites obtained and tested from three mines) and three application rates (4:100, 12:100, 20:100 - dry weight compared to the extracts of the control (Figure 1a).

5) Cumulatively, more lead was extracted from the Bunker Hill soil amended with the CH zeolite than from the control. These differences were significant at the 95 percent confidence level. Extracts of two XY treated soils, 4:100 and 20:100 mix ratios, and the extracts of limestone-amended soils had significantly lower cumulative lead values than extracts of the controls. Extracts of the XY treated soil mixed in a 12:100 mix ratio were not significantly different than the control (Figure 1a).

6) Cumulative lead values in extracts of soils amended with limestone were significantly (95% confidence level) lower than those in extracts of soils amended with the CH zeolite and the XY 12:100 mixes. The cumulative lead values in the XY 4:100 and 20:100 mixes were not statistically different from those in limestone extracts (Figure 1a).

7) Both CH and XY zeolites effected a reduction of 50 percent or more in the concentration of lead in the first MWEP extracts as compared with the controls. This observation is consistent with the MWEP results obtained during the screening test program (Figure 1a).

8) On a cumulative basis, zinc and cadmium values were statistically lower in all four sequential extracts of CH, XY, and limestone-amended soils as compared with extracts of control samples (Figures 2a and 3a). The extracts of CH and XY amended soils (except the XY 4:100 mix) contained significantly less cadmium than did the extracts of the limestone amended soils; the XY 4:100 mix was not statistically different from the limestone.

Permeameter Seepage Program

The seepage from the permeameters (Fig. 4) used to determine hydraulic conductivity was analyzed to determine concentrations of target metals released with time and the cumulative amount released during the determinations. The conclusions drawn from these tests are summarized as follows:

1) Concentrations of lead and zinc in seepage from the test permeameters (Figures 1b and 2b) corresponded with the results of the water leach tests (Figures 1a and 2a). Cadmium in the permeameter effluents (Figure 3b) was not consistent with its concentrations in MWEP extracts (Figure 3a).

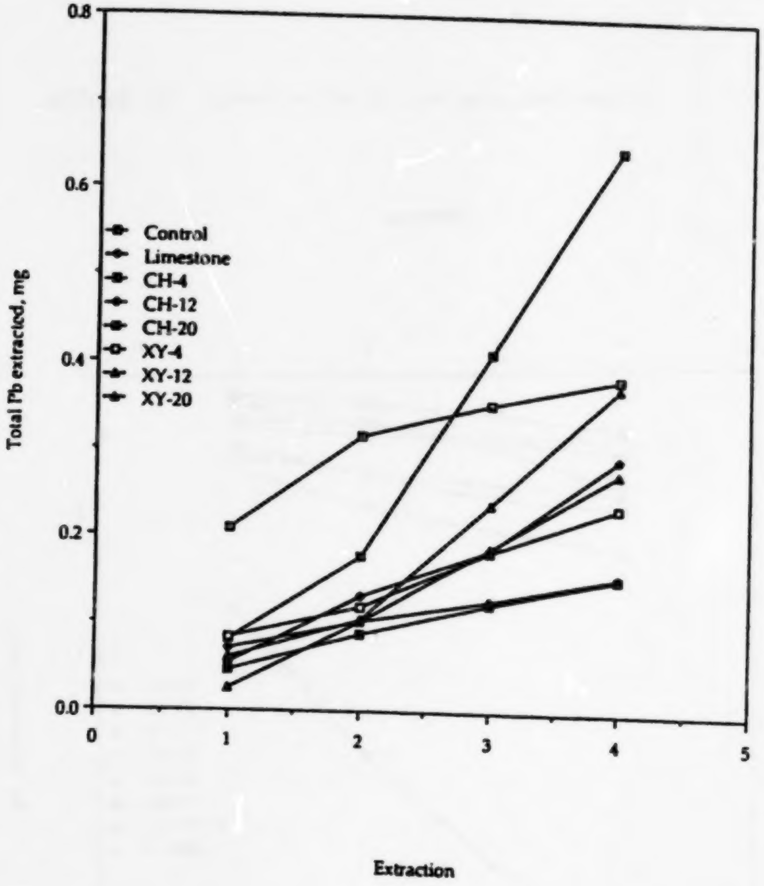

FIGURE 1a. Cumulative Pb in MWEP extracts.

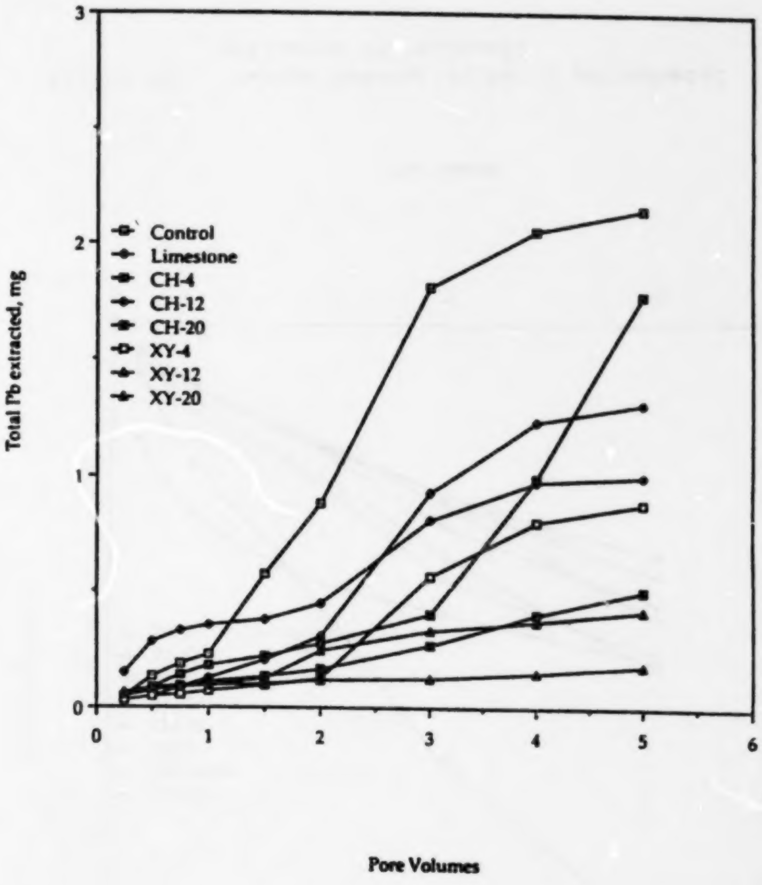

FIGURE 1b. Average cumulative Pb in permeameter effuluets (normalized).

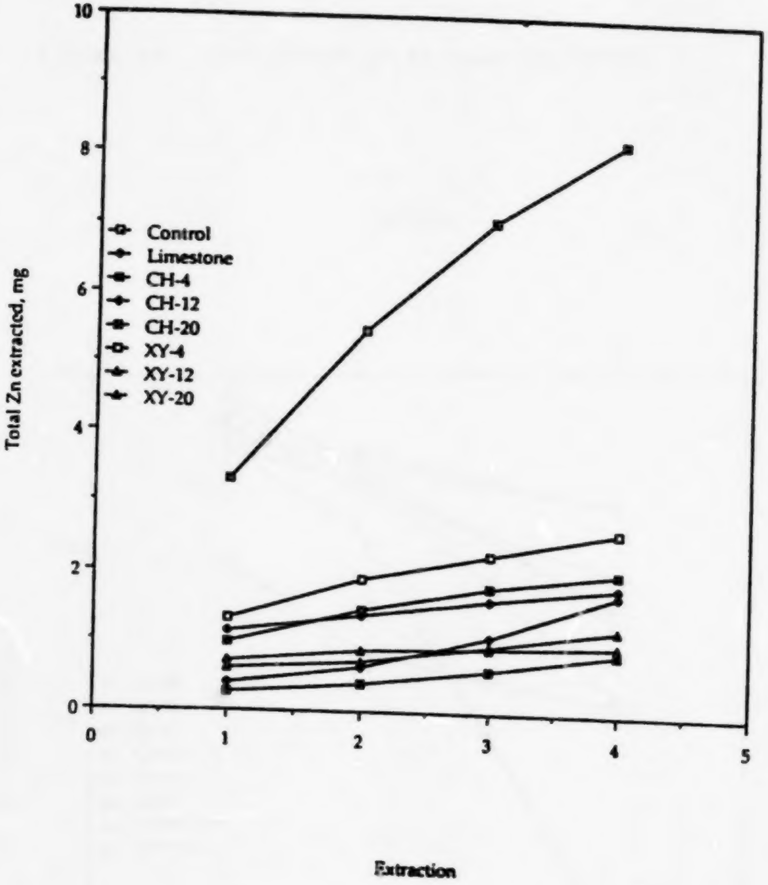

FIGURE 2a. Cumulative Zn in MWEP extracts.

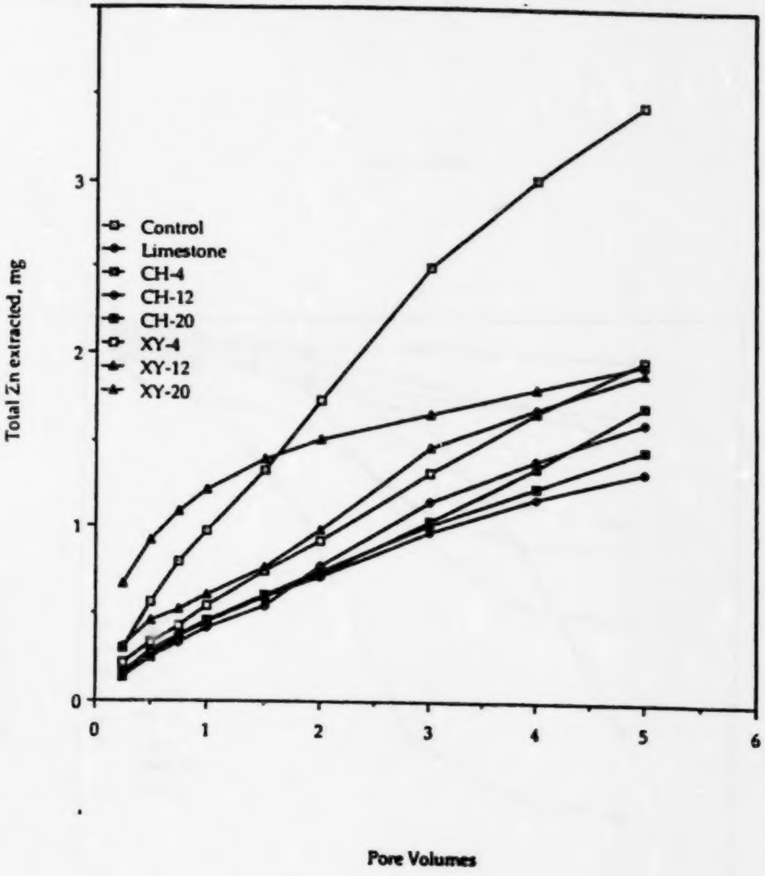

Figure 2b. Average cumulative Zn in permeameter effluents (normalized).

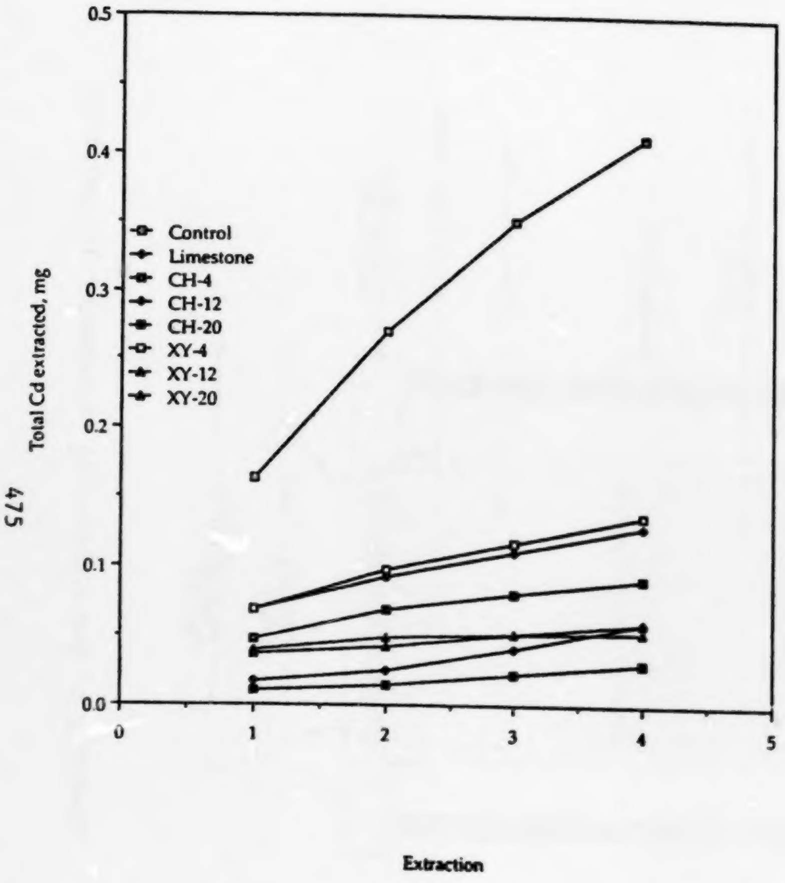

FIGURE 3a. Cumulative Cd in MWEP extracts.

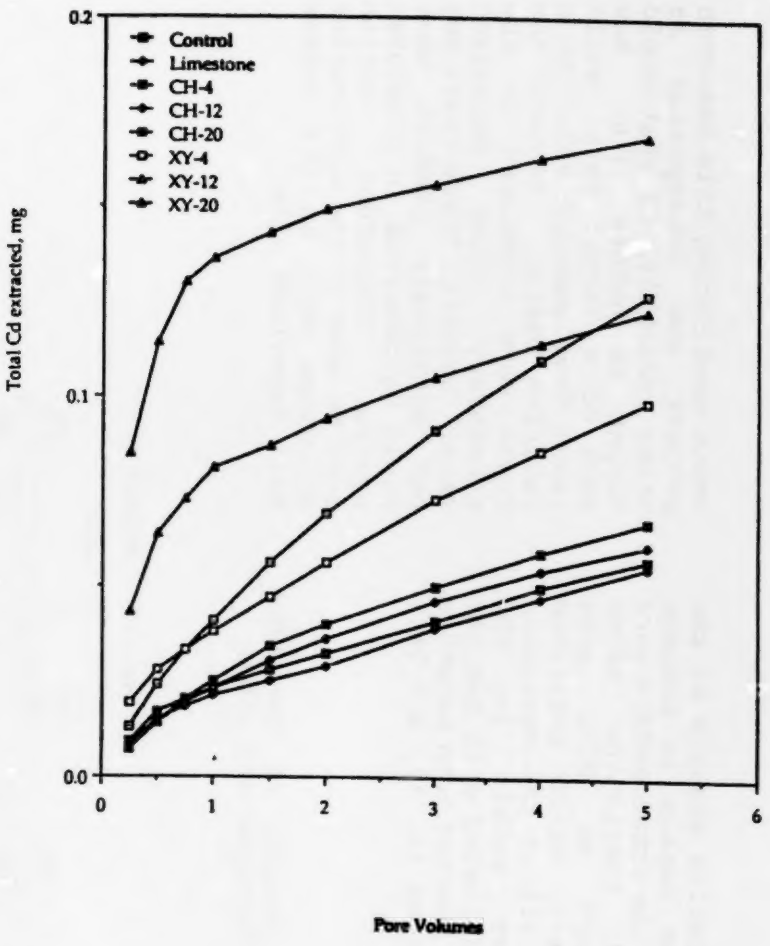

FIGURE 3b. Average cumulative Cd in permeameter effluents (normalized).

2) Cumulative amounts of the target metals in seepage from the permeameters were still increasing after passage of five pore volumes, which indicated that all of the available target metals in the contaminated soil had not been leached into solution (Figures 1b, 2b, and 3b).

CLOSURE

The results of the MWEP water extractions and other tests used during this research project are interpreted as being indicative of what would happen in nature (i.e., how much of a target metal would leach from amended soils on a relative basis). Because the tests were conducted in the laboratory using deionized water, however, these tests may not accurately predict what would be observed in a natural system. Therefore, caution must be used in the application of these data to the Bunker Hill Superfund site.

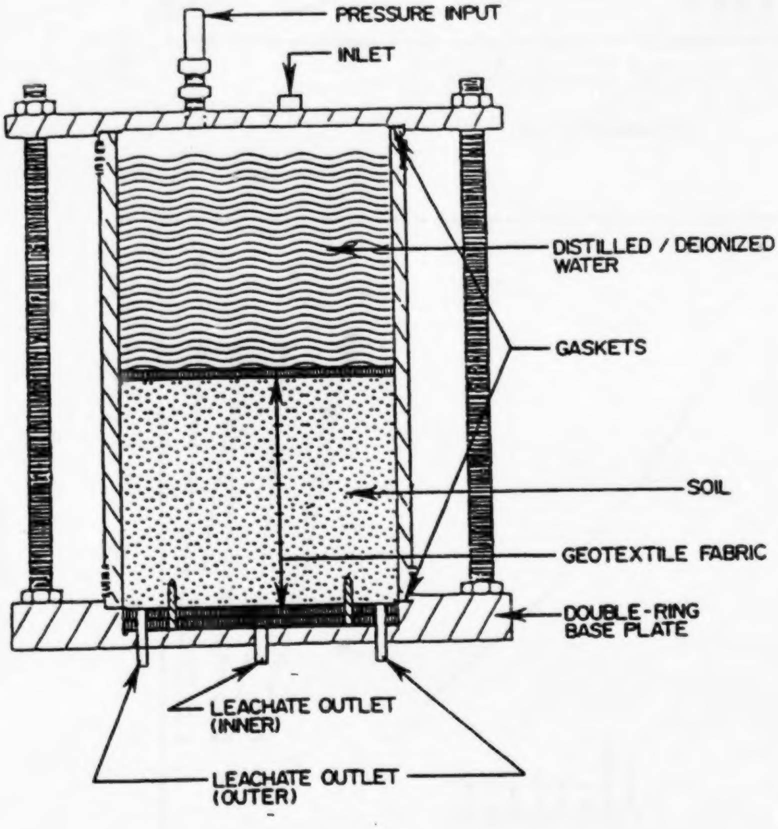
PRESSURE INPUT
INLET
DISTILLED / DEIONIZED WATER
GASKETS
SOIL
GEOTEXTILE FABRIC
DOUBLE-RING BASE PLATE
LEACHATE OUTLET (INNER)
LEACHATE OUTLET (OUTER)

Figure 4. Schematic of the double-ring permeameter in operation.

ACKNOWLEDGEMENTS

The project described in this paper was part of a complex undertaking that required the cooperation and coordination of a multidisciplinary team of research scientists and engineers. Mr. John Barich of EPA Region X originated the request for technical assistance to RREL for the evaluation of natural zeolites as soil amendments and led the EPA personnel that collected the soil samples from both the Bunker Hill Superfund site and the United Chrome Products, Inc. Superfund site. Mr. Daniel Krawczyk of EPA's Corvallis Environmental Research Laboratory (CERL) in Corvallis, Oregon, provided rapid turnaround analytical support for this program by conducting the analyses of metals in numerous samples. Their contributions to the successful completion of this project are recognized and appreciated.

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

TREATMENT OF WATER REACTIVE WASTES

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ABSTRACT

In Europe there is a small but growing amount of water reactive waste. These wastes (e.g. titanium tetrachloride) react violently with water to produce huge quantities of hydrogen chloride. They therefore pose a serious waste disposal problem because conventional treatment methods are not suitable. In addition to their reactivity these wastes pose a number of other problems, namely; they are often contaminated with halogenated organic chemicals which cause the waste to form a sludge, the waste is almost always packed in 200 litre drums, and finally it is potentially a very corrosive mixture.

Lanstar Wimpey Waste was approached by a number of companies to see if we could treat this kind of waste so a laboratory project was undertaken and when this produced encouraging results the process was scaled up to a pilot plant that was capable of handling full 200 litre drums. The results of this pilot plant work are discussed in this paper. In essence the process involves; homogenisation of the waste, hydrolysis, phase separation, neutralisation of organic and aqueous layers, incineration of organic solvents, dewatering of the neutralised aqueous slurry with the filter cake going to a clay containment landfill site and the filtrate going to a sewerage works.

This process ensures that these types of wastes are disposed of by the Best Practicable Environmental Option.

INTRODUCTION

The European chemical and fibre optic industries produce chemical wastes that are water reactive. Typical wastes are titanium tetrachloride, antimony pentachloride and phosphorous oxychloride. These wastes react violently with water releasing huge quantities of hydrogen chloride. This type of waste is produced in small but regular quantities and almost always in 200 litre drums. In its most difficult state the waste is produced by the organic chemical industry as a spent catalyst. In this form the waste contains halogenated hydrocarbons that often form a sludge in the bottom of the drum.

Conventional disposal methods such as landfilling, incineration, and chemical neutralisation are inappropriate for this type of waste. For instance, landfilling of liquids in drums is simply not allowed in the U.K., incineration of predominantly reactive inorganic wastes is not recommended, whilst direct neutralisation of such wastes is not possible due to the generation of vast quantities of hydrogen chloride.

In 1987 detailed laboratory investigations were under-taken to determine whether it was possible to: (a) perform controlled hydrolyses on such wastes, (b) treat the products of the hydrolyses.

Following successful laboratory treatment of a number of wastes it was decided to do some pilot plant work on full drums. This paper is a report on these trials.

PURPOSE

The purpose of this project was to develop a commercially viable process for the hydrolysis and subsequent treatment of water reactive wastes. Whilst the main emphasis was placed upon the hydrolysis reaction the whole project also depended upon there being disposal routes for the acids and organic solvents generated. It was hoped that these disposal routes would exist 'in house'.

APPROACH

Best Practicable Environmental Option

The Company is committed to finding the Best Practicable Environmental Option for any given waste. This means analysing the costs and benefits of different waste disposal options for a given waste so that the greatest pollution abatement will be given for the minimum costs. So the first approach was to see whether this category of water reactive wastes could be fitted into any of the Company's existing portfolio of treatments. These were; chemical treatment (neutralisation, oxidation, reduction, etc.), physical treatment (filtration, centrifugation, distillation, etc.), biological treatment, incineration or landfill.

When it became apparent that these wastes required pre-treatment prior to other disposal methods coming into play a laboratory investigation was undertaken.

Laboratory Investigation

A known weight of water was added to a 2 litre reaction vessel. The waste in question was added, under gravity, at a known rate whilst the temperature was continually monitored. Periodically small quantities were removed from the reaction vessel to determine acid strength. All hydrogen chloride fumes were vented from the reaction vessel and scrubbed.

Initially only inorganic wastes that were completely liquid, e.g. titanium tetrachloride, underwent this evaluation. However, as a routine process was developed more difficult wastes were tested, notably those that were contaminated with halogenated solvents.

In all cases, when a waste was successfully hydrolysed in the laboratory it was then tested to determine if it could then be processed through existing processes. The key thing was to evaluate whether the waste could go through the normal acid neutralisation process. Thus, the following questions required answering: Could neutralised sludge be dewatered, was the filter cake acceptable for landfill and was the water acceptable for sewer discharge?

From this work a standard method of operation was developed in which the initial charge of water was fixed, the final concentration of hydrochloric acid selected and a rate of addition recommended.

Pilot Plant Evaluation

The recommendations of the laboratory investigation were taken to the pilot plant. This plant consisted of a 2,250 litre glass lined reactor fitted with cooling water and connected to a packed column caustic scrubber (normal operating strength 10%).

During this evaluation trials with one or two drums were undertaken. The process followed the laboratory trials. Thus a known volume of towns water was charged to the reactor, during the addition of the waste (again under gravity) the temperature and the weight of the drum were continually monitored. Furthermore, the strength of the caustic in the scrubber was measured at regular intervals.

PROBLEMS ENCOUNTERED

Drums

These wastes are so reactive that as a protective measure they are transported in overdrums. Thus a foolproof system for removing the drums from their overdrums and delivering them to the treatment plant was essential. The drums, though often new drums, could not be considered pressure vessels and therefore the contents had to be fed to the reactor by gravity. This meant firmly fixing the drums in a stillage. In order to aid this process dry nitrogen was bubbled through the liquor but in such a way that no pressure build-up occurred. N.B. Nitrogen was introduced through a specially designed adaptor which kept the pipe to the reactor free from sludge build-up.

A major difficulty occurred with those wastes that had been catalysts in the organic chemical industry. In this case there was always some sludge formation in the bottom of the drum. Generally this was overcome by rolling the drum for 30 minutes prior to fixing the drum in its stillage. However, for particularly awkward drums, when most of the liquid had been removed from the drums a dry chlorinated solvent (such as perchloroethylene) was added to the drum which was rolled and then re-fitted to the stillage.

In all cases the drums were completely emptied (checked by weighing and dipping) before being quenched with water, re-emptied and crushed.

Due to dealing with drums there was always the problem of continually coupling and decoupling lines between the drum and reactor. This always produced fumes of hydrogen chloride and to prevent this being a problem there was a vent over the reactor and drum that fed straight into the scrubber system.

Reactivity

The wastes in question are

so reactive it is essential to have an adequately sized scrubber to cope with all the hydrogen chloride generated.

Also, in those instances where there are organic chemicals present the lining of the reactor and holding tank is of prime importance. In fact, with one particular waste there were chlorofluorocarbons present with the result that on hydrolysis a small quantity of hydrofluoric acid was produced. In order to minimise the affect of this aggresive acid calcium chloride was added to the water prior to the hydrolysis reaction so that during the reaction calcium fluoride would precipitate, but this did not minimise the care needed about choosing the reactor linings for these kinds of waste.

Acid Strength

Experience has shown that the optimum acid strength is around 15% w/w. At this concentration all the waste goes into solution. At higher concentrations a slurry is sometimes produced. Furthermore, at 15% strength the acid waste can be directly neutralised with 10% calcium hydroxide slurry and the resulting slurry remains pumpable. At greater than 15% acid strength it has sometimes been found necessary to dilute the acid.

When the acid strength is maintained around 15% the temperature is always maintained less than 50°C. A maximum operating temperature of 70°C is therefore used as a control guard against 'unusual reaction' and to prevent an overload on the scrubber system.

Phase Separation

This problem only arose with those wastes containing separable organics but in this case it was essential to have a phase separation tank. As the organics were never present in large quantities it was always possible to draw off 'clean' acid from the holding tank whilst allowing a build-up of organics on top of the tank.

However, on removing the organic layer it was always found to be acidic. This meant neutralisation with sodium hydroxide in a separate reactor followed again by phase separation. However, because this was only needed infrequently both processes were done in the same reactor.

The neutralised organic layer then went for incineration whilst the neutralised aqueous layer was processed with other waste acids being treated on site.

RESULTS

All the results are from pilot plant studies.

Typical Reactions

$$TiCl_4 + 2H_2O \longrightarrow TiO_2 + 4HCl$$

$$2HCl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O$$

The Process

Figure 1 shows the block flow diagram for water reactive wastes. Experience has shown that the following are the parameters that give the best results:-

Hydrolysis

Drum rolling - 30 minutes

Water charge to the reactor (2250 litres) - 1400 litres

Rate of addition of waste to reactor - 5 litre/minute

Typical time to empty 200 litre drum (see Figure 2) - 70 minutes

Maximum number of 200 litre drums processed per batch - 2

Maximum operating temperature - 70°C

Typical operating temperature - 35°C (see Figure 3)

Solvent for washing organic sludges - perchloroethylene

Maximum acid strength - 20% w/w as HCl

Typical acid strength - 15% w/w as HCl

Neutralisation

Neutralisation medium for the acid layer - calcium hydroxide

Dewatering equipment- Vacuum belt filters

Total chlorinated hydrocarbons in filtrate - less than 100 microgram/ltr

Landfill of filter cake - Site has minimum of 8 metres of clay

Incineration of solvents:

Temperature : 1200°C

Oxygen : Excess

Time in flare: Greater than 1 second

N.B. The solvents are currently incinerated at sea. It is more than likely that between 1992 and 1994 the solvents will be transferred to a landbased incinerator.

Based upon this work done on the pilot plant and the fact that there is a need in the U.K. for this method of processing a decision has been taken to install a 9,000 litre reactor. This will operate on the regular work whilst the pilot plant will continue to operate on 'spot' work and, of course, further development work.

The plant has gone through a full Hazop process and a full set of operating instructions have been issued.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

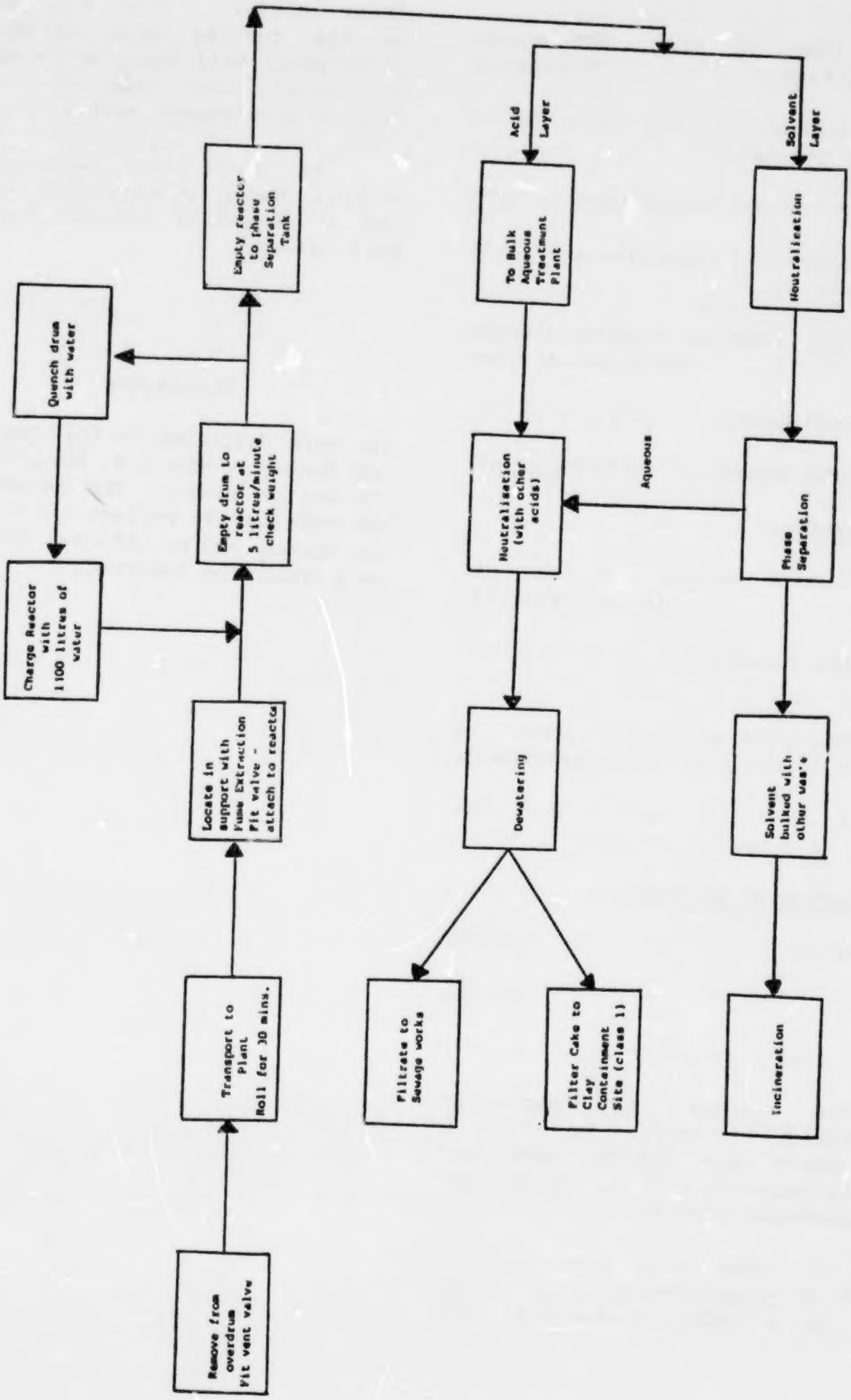
Remove from overdrum Fit vent valve
Transport to Plant Roll for 30 mins.
Locate in support with Fume Extraction Fit valve - attach to reactor
Charge Reactor with 1100 litres of water
Empty drum to reactor at 5 litres/minute check weight
Quench drum with water
Empty reactor to phase Separation Tank
Acid Layer
Solvent Layer
To Bulk Aqueous Treatment Plant
Neutralisation
Neutralisation (with other acids)
Aqueous
Phase Separation
Dewatering
Solvent bulked with other wastes
Filtrate to Sewage works
Filter Cake to Clay Containment Site (class 1)
Incineration

FIGURE 1. WASTE FLOW DIAGRAM FOR WATER REACTIVE WASTES

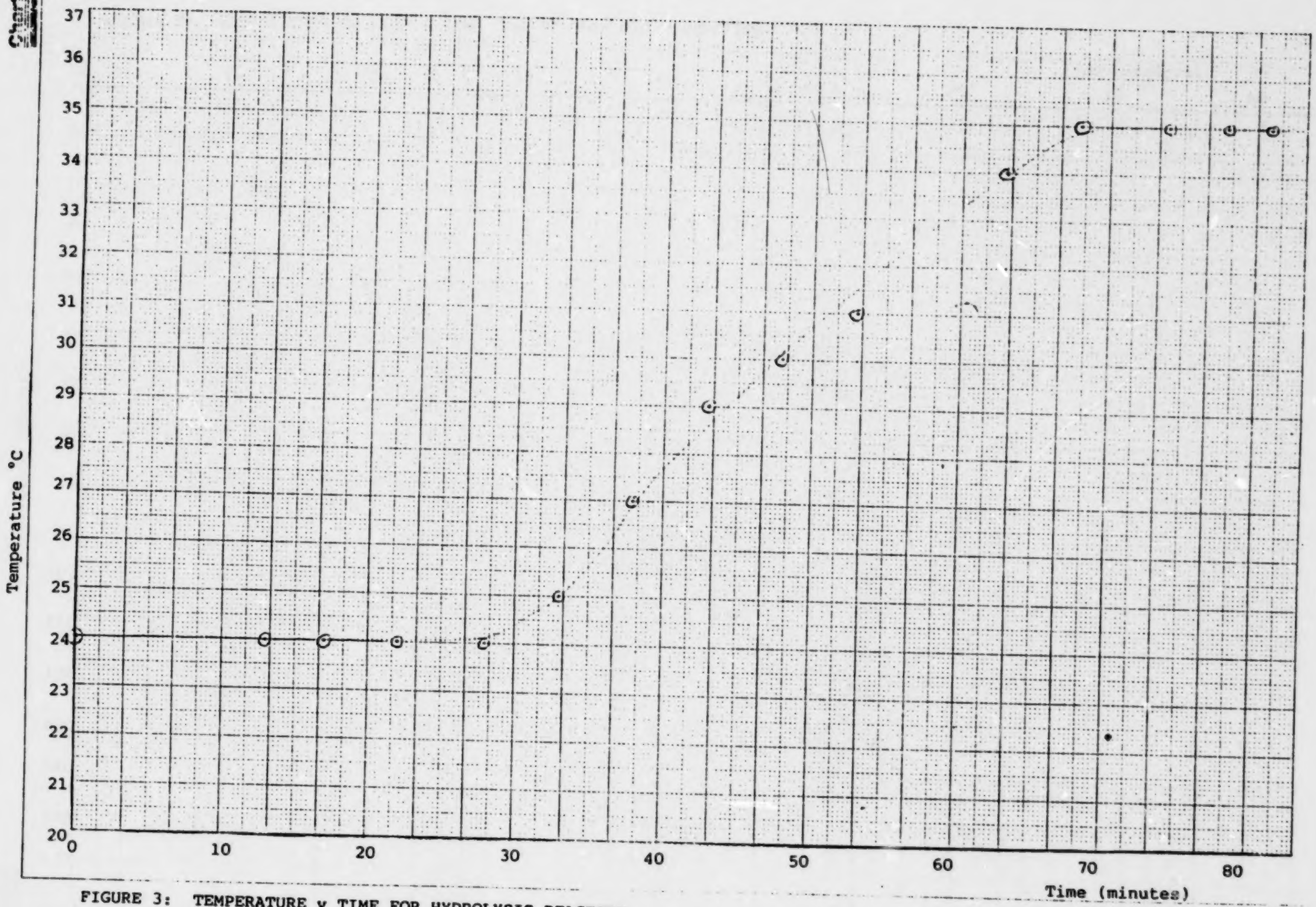

FIGURE 3: TEMPERATURE v TIME FOR HYDROLYSIS REACTION

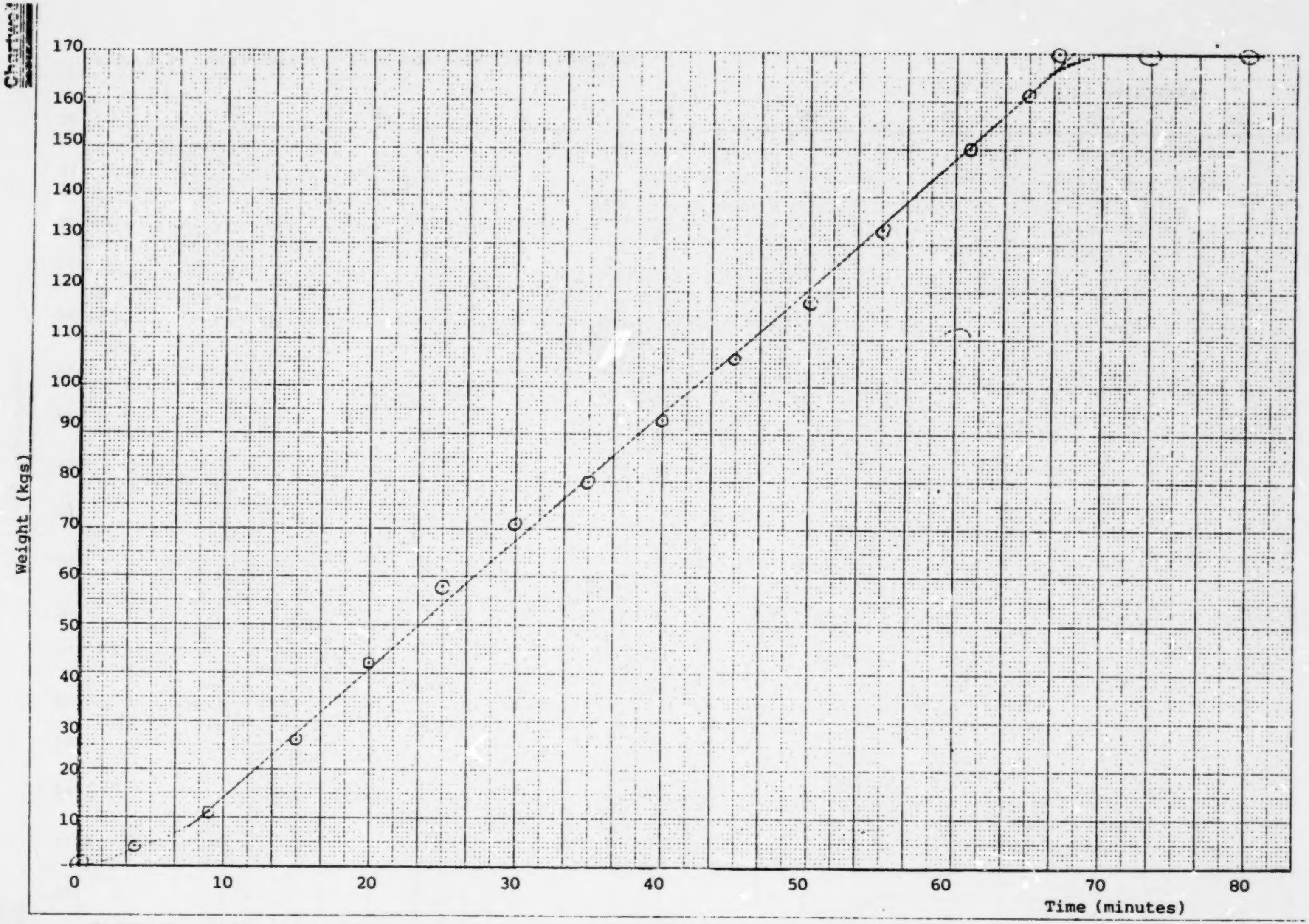

FIGURE 2: WEIGHT LOSS OF DRUM v TIME DURING HYDROLYSIS REACTION

USE OF INNOVATIVE FREEZING TECHNIQUE FOR IN-SITU TREATMENT OF CONTAMINATED SOILS

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ABSTRACT

In the past few years, CRREL has been investigating the use of artificial freezing as an innovative technique for soil decontamination. A preliminary laboratory study was conducted specifically to evaluate and analyze the possibility of mobilizing different types of contaminants by freezing in Lebanon silt. Contaminants investigated were explosive residues most extensively found at the U.S. Army ammunition plants as well as volatile organic compounds (VOCs), such as chloroform and toluene. Explosives studied were 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 2,6-dinitrotoluene (2,6-DNT), ortho-nitrotoluene (O-NT), and meta-nitrotoluene (M-NT).

Preliminary data from the laboratory column studies suggested that there was a certain degree of movement of both explosives and VOCs when soil columns of Lebanon silt saturated with these contaminants were frozen unidirectionally from the bottom up. Slopes of the control and frozen soil concentration profiles were statistically analyzed and a comparison between them was made. One freeze cycle at an average freezing rate of 0.5 cm/day was used. Insignificant amounts of movement (< 10% change) were observed for RDX, HMX and TNT. Relatively greater movements (20–40% change) were observed for 2,6 DNT, O-NT, M-NT, toluene and chloroform. For given freezing rate, freeze-thaw cycles, soil and moisture content, it was hypothesized from this and other previous experimental data that the ability to move any contaminant by freezing strongly depends on the type, initial concentration level and the soil/chemical interaction of the contaminant.

INTRODUCTION

Several military bases and U. S. Army ammunition plants have soils and sediments contaminated with explosive residues resulting from the manufacture, use, and disposal of organic-based explosives. Some of the explosive compounds include TNT, RDX, HMX, 2,6-DNT, M-NT and O-NT. These military facilities and other industrial sites contain VOC contaminants in addition to explosive residues. Cost-effective and safe control, treatment and disposal of hazardous/toxic wastes remain as some of the major environmental problems and challenges facing the U.S. and other industrialized countries. In particular, the transport of the contaminants to ground and surface water is perhaps the main issue of public concern. Iskandar and Houthoofd (1) and Iskandar and Jenkins (2) summarized the review of available techniques for remedial action at uncontrolled hazardous waste sites, and concluded that current techniques are neither adequate nor cost-effective for protecting ground and surface water.

Artificial freezing is being studied as a means to decontaminate explosives- and VOCs-contaminated soils and may have the potential to be a cost effective, environmentally safe, and readily implemented technology.

PURPOSE

In the past decade, the growing problem of hazardous wastes has contributed to a recent increase in the public awareness and preference for a research effort in developing new cleanup technology with a minimum negative impact on the environment and surrounding aesthetics. Consequently, there is an urgent need for continued research to investigate other possible innovative and cost-effective techniques for treating and controlling hazardous/toxic wastes. Iskandar et al. (3) and Ayorinde et al. (4) have evaluated laboratory methods for the potential use of artificial freezing to decontaminate soils contaminated with VOCs and their data indicated moderate success. Perry and Ayorinde (5) and Taylor (6) have experimentally demonstrated that different types of explosive residues can be effectively moved in water by freezing.

The purpose of this paper is to present the preliminary results of a laboratory investigation of exploring artificial freezing as an innovative potential technique for in-situ soil decontamination. In particular, the paper describes and summarizes the experimental approach and analysis developed for a laboratory column study to evaluate possible freezing-induced transport of volatile and nonvolatile contaminants in soil.

APPROACH

The test apparatus used consisted of 7-cm-OD by 0.325-cm-thick by 12.5-cm-high Lucite cells for containing Lebanon silt, an environmental chamber for housing the soil columns and for controlling ambient temperature, a backsaturation test setup, a 2-L carboy for preparing contaminant concentration, thermocouples, sampling tools, programmable cooling baths (each with rapid response time and a temperature ramp controller), sample storage facilities, an oven and an analytical laboratory for conducting high-performance liquid chromatography (HPLC). Each Lucite cell was fabricated and carefully fitted with aluminum end caps and stainless steel inlet and outlet ports at the bottom and top, respectively. Polyethylene filters, 0.5 cm in thickness, were also placed at the top and bottom of the cell. The Lucite cell was also instrumented with type T (copper-constantan) thermocouples for monitoring temperature during freezing.

Sample Preparation:

Because of both the unknown complex chemical behavior of organic compounds, and the undefined potential interaction between different types of volatile and nonvolatile organic compounds under low temperature conditions, the explosive compounds were separated from the VOCs for our investigation. At the time of the experiment, there was no information in the literature about any possible chemical interaction when explosive residues and VOCs are mixed together to produce a spike solution. To avoid any additional complexity, separate soil sample columns were prepared for the explosives and the VOCs. Since then, the in-house CRREL organic chemistry group (Jenkins [7]) has noted that no adverse chemical reactions occur when mixing solutions containing explosive compounds and VOCs. This assessment agrees with the conclusion of a study conducted by Karickhoff et al. (8).

Eight sample columns were prepared. Two columns were used as controls for the VOC (column A) and the explosive contaminants (column E), respectively. Three columns (columns F, G and H) were used as replicates for the explosive-contaminated soil while the remaining three columns (columns B, C, and D) were replicates for the VOC-contaminated soil. Each Lucite column was packed with oven-dried Lebanon silt to an average density of 1.67 g/cm^3 and a porosity of about 36%. The packing was done in 2-cm layer lifts to achieve relatively uniform density throughout the column. Once the test cell was full, an end cap was placed with the filter on top of the soil, and the cell was sealed. Both the bottom inlet and the top outlet were then attached with three-way control valves fitted with Teflon tubing. A typical Lucite test cell used for the experiment is shown in Figure 1 with a soil sample height of 12 cm.

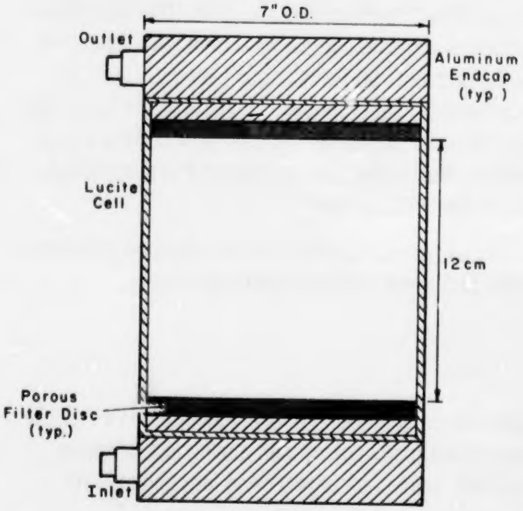

Figure 1. Typical Lucite soil test cell.

Preparation of Contaminant Spike Solutions:

The VOC spike solution consisting of chloroform and toluene was prepared and their concentrations were determined in accordance with the previously established procedures (Ayorinde et al. [4]). The expected concentrations for chloroform and toluene were 990 and 230 mg/L, respectively. Explosive residues were added to 200 mL of Milli-Q water and the resulting solution was poured into a 2-L carboy in which the solution was mechanically mixed for about 24 hours. The expected concentration for each of the explosive residues was 20 mg/L. Before backsaturating the soil columns with the spike solution, the VOC contaminant concentrations were 604 and 84 mg/L for chloroform and toluene, respectively, and about 10 mg/L for each of the explosive contaminants.

Backsaturation Method and Breakthrough Curve Procedure:

To obtain a reasonably uniform distribution of the contaminant concentration through each soil column prior to freezing, each column was backsaturated with 10 pore volumes of spike solution. An increment of 0.5 pore volume was used until a total of 10 pore volumes was reached. The backsaturation apparatus used is shown in Figure 2. The burette with the spike solution was connected to the Lucite soil columns using the Teflon tubing to form a closed loop as shown in Figure 2. The burette was placed high above the soil columns to provide enough head to move the spike solution very slowly through the soil from the bottom up. Two of the eight prepared soil columns were simultaneously backsaturated at each time. During the backsaturation of a new set of soil columns, already saturated columns were kept inside the environmental chamber. The effluent solution from each column outlet was collected in a closed overflow flask to minimize volatilization of the VOCs.

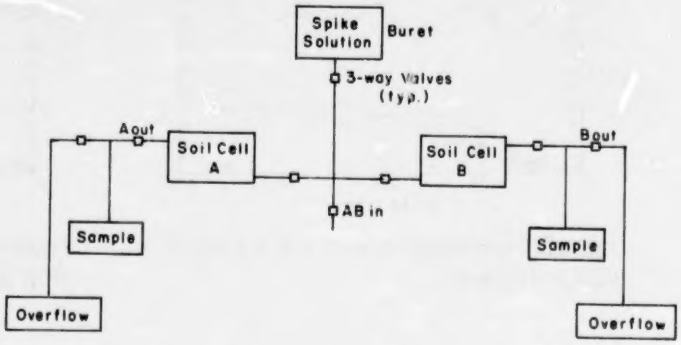

Figure 2. Backsaturation apparatus.

For each incremental pore volume, the inlet solution at the bottom of each soil column and the outlet solution at the top of the column were continuously monitored and collected for chemical analysis. HPLC was used to measure the concentration levels of the explosive residues and VOCs in the collected solution based upon the procedure developed for determining nitroaromatics and nitramines (Jenkins et al. [9]) and VOCs (Jenkins [7]) in water. As shown schematically in Figure 2, the inlet solution from the burette is identified as AB_{in}, while the effluent solution coming out of samples A and B is identified as A_{out} and B_{out}, respectively. Examples of typical breakthrough curves obtained for all the contaminants studied are shown in Figures 3 and 4 for RDX, toluene, M-NT and O-NT.

The soil was assumed to be fully saturated after a flow of 10 pore volumes of the spike solution, and both the inlet and outlet valves for columns were closed. The soil sample columns were then placed in the environmental chamber for subsequent freezing. The backsaturation apparatus with a closed loop system depicted in Figure 2 was developed as a rational method of minimizing the complex problem of the volatilization losses of the spiked VOCs while saturating the soil samples.

Sample Freezing and Sampling Methods:

The environmental chamber which housed the eight saturated soil columns was set at +1.0°C and maintained at this temperature throughout the experiment. Prior to freezing, all the soil columns were equilibrated at +1.0°C for 48 hours. Soil columns B, C, D, F, G, and H were then placed on a large cooling plate inside the environmental chamber. Control columns A and E, kept unfrozen throughout the test, were placed on top of an insulation pad and

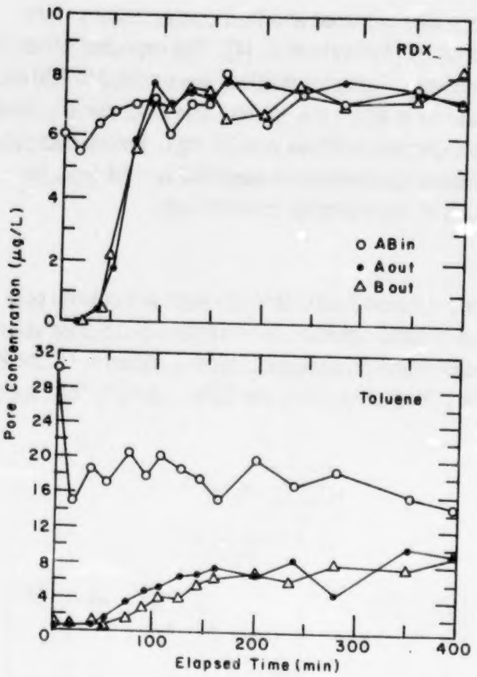

Figure 3. Breakthrough curves (conc. vs time) for RDX and toluene.

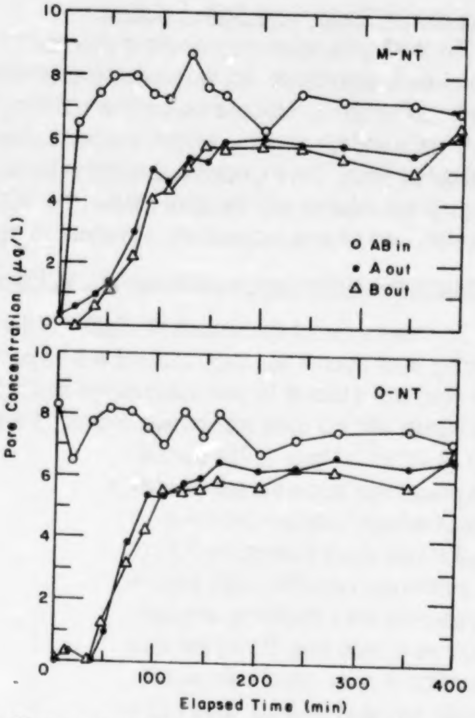

Figure 4. Breakthrough curves (conc. vs time) for M-NT and O-NT.

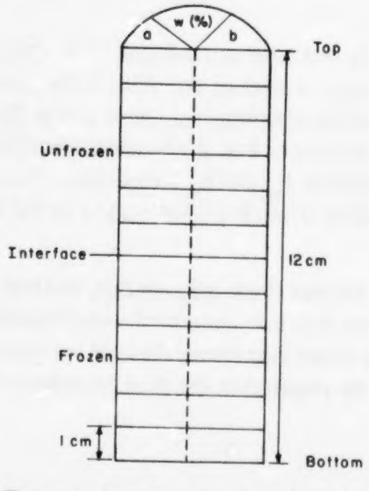
w (%)
a
b
Top
Unfrozen
Interface
12 cm
Frozen
1 cm
Bottom

Figure 5. Sampling layout of half soil column after flash-frozen in liquid nitrogen.

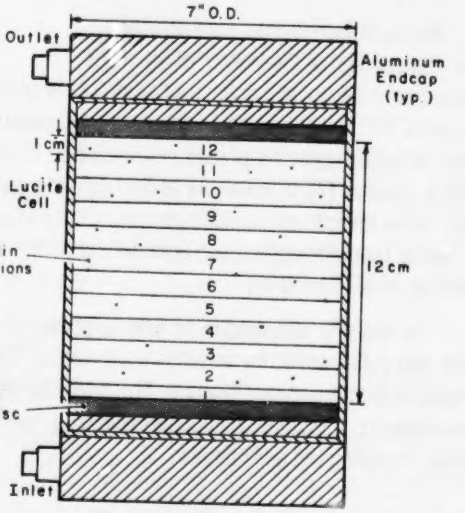
7" O.D.
Outlet
Aluminum Endcap (typ.)
1 cm
12
11
10
9
8
7
6
5
4
3
2
Lucite Cell
Thin Sections
12 cm
Porous Filter Disc (typ.)
Inlet

Figure 6. Test cell soil sampling scheme with thin section dimensions.

isolated from the bottom cooling plate. Then, another large cooling plate maintained at the inside chamber temperature of +1.0°C was placed on the top of the eight columns to control the top end boundary temperatures of the soil columns. The temperature data for the cooling baths, the environmental chamber, and the soil column thermocouples were collected on a DIGI III datalogger, interfaced with an IBM PC.

The top and bottom boundary temperatures of the soil columns, as well as the environmental chamber temperature were controlled by programmable cooling baths. These programmable cooling baths are capable of maintaining temperatures within 0.1°C. The freezing of the soil columns was gradual and was from bottom up in order to eliminate the possible effect of gravity on the mobility of contaminants. By controlling the cooling rate of the bottom plate at a constant temperature decrement rate of about 0.4°C per day to freeze the soil columns, an approximate freeze rate of 0.5 cm/day was achieved. Because of the good temperature control of the environmental chamber, a one-dimensional vertical freezing of the soil columns was also achieved. Columns B, C, D, F, G and H were frozen approximately halfway (6 cm) from the bottom.

At the end of the freezing process, all samples were taken out of the environmental chamber and flash frozen in liquid nitrogen. Thin sectioning was used to provide estimation of the sample soil solute concentration profiles. Frozen soil columns were transferred to a coldroom and cut vertically in half as shown in Figure 5. One half was kept in the freezer, while the other was cut into 1-cm-thick sections on a band saw as depicted in Figure 6.

Two sample duplicates of each thin section were obtained, representing about 2/3 of each thin section made from 1/2 of the original sample. The remaining 1/3 of the thin section was used for estimating the sample moisture content profile. The thin-section sample duplicates were placed in sealed glass scintillation vials to be extracted for chemical analysis. About one milliliter of the extract was then transferred into mini-autosampler vials for direct concentration determination using HPLC. By this procedure, the concentration profile of the contaminants along each soil column was obtained.

PROBLEMS ENCOUNTERED

One of the problems concerned the difficulty in achieving initial uniform distribution of the contaminants in soil. There were several contributing factors. These included the inherent soil inhomogeneity, flow tortuosity, local soil/contaminant interactions due to sorption and other chemical and physical forces, and local losses by absorption, biodegradation and volatilization. Since these influencing parameters could not be completely eliminated, the experiment was designed to include controls. To minimize the abovementioned contributing factors, triplicate soil columns were used for freezing treatment with duplicate samples taken at different locations along each column height. Other problems centered on the limitation in obtaining and chemically analyzing a large number of soil samples in a timely and efficient way that would be representative of the soil columns for the experiment. It was only possible to analyze about 1/3 of each column for contaminant concentration determination. The underlying assumption was that the soil sample was relatively homogeneous without (a) any local preferential sorption of the contaminants to the soil, (b) any significant tortuosity, and (c) appreciable accumulation of any of the contaminants in the soil portion used for the moisture content estimation.

RESULTS

Data Analysis

Theoretical analysis of freezing-induced organic contaminant transport in soils requires, in general, the use of advective-dispersive equations with sorption and volatility effects coupled with heat transfer with phase change. The set of equations involved here is very complex and difficult to analyze. However, in order to model the transport of organic compounds in soils due to freezing, this type of complex coupled equations would have to be developed and solved. In this paper, no attempt is made to develop an analytical model for the data presented. Such an effort is included in our research investigation in the future. Our current research goal is to develop reliable experimental methods for obtaining data that can be used for developing and testing models that describe freezing-induced contaminant transport in soils.

As noted above, there were two duplicate concentration measurements at each location along each soil column. Duplicate analysis using Youden's Method (Bauer [9]) was used for all measured data. Thus, at each location along each soil column,

$$C_f = \text{mean}(\Sigma\ [C^F_f(i) + C^G_f(i) + C^H_f(i)]\ )\ \ ; i = 1 \text{ to } 2 \tag{1}$$

$$C_t = \text{mean}(\Sigma C^E_t(i))\ \ ;\ i = 1 \text{ to } 2 \tag{2}$$

where i represents the number of duplicates per location along the soil column, and f and t subscripts denote frozen and thawed (unfrozen) soil columns, respectively.

The standard deviation (STD) and the corresponding coefficient of variation (CV) for the measured concentration at each location along each soil column were then calculated using Equations 1 and 2. Thus:

$$STD = (\Sigma\ [(c_{f \text{ or } t}(j) - C_{f \text{ or } t})^2]\ /(N-1))^{1/2}\ ; j = 1 \text{ to } 6 \tag{3}$$

for subscript f and j = 1 to 2 for subscript t

$$CV(\%) = 100 \times STD/C_{t \text{ or } f} \tag{4}$$

where N is the number of data measurement locations along the soil column.

In an attempt to minimize inherent variability in the measured data arising from unavoidable variations in measurement, sampling, sample preparation and soil properties (e. g., heterogeneity), the concentration value per location along each column was normalized with respect to the mean concentration value (C_{tmean}) for the whole height of the unfrozen control column E. Hence,

$$(C_{tmean}) = (1/N)\Sigma C^E_t(k)\ ;\ k = 1...N \tag{5}$$

where N is the number of data measurement locations along the unfrozen control column E. And the normalized concentration for the soil column profile is given by

$$\text{Normalized Conc.} = C_{t \text{ or } f}/C_{tmean} \tag{6}$$

As indicated above, the purpose of this preliminary experimental investigation was based on the hypothesis that freezing can move organic contaminants in soils just as it has been demonstrated for water (Perry and Ayorinde [5], Taylor [6]). To test this hypothesis, two simple analytical approaches were adopted to analyze the measured concentration data.

The first approach compared the average of the concentration profile for the frozen bottom half (0-6 cm) of the freezing-treated columns (columns F, G and H) with the corresponding average concentration for the bottom half (0–6 cm) of the unfrozen control column (column E). As it may be recalled, it was pointed out earlier that the columns F, G and H which were subjected to freezing only froze to about 6 cm from the cold bottom ends of the columns. The bottom-half average calculated concentration was each normalized with respect to Ct_{mea}. The difference between the frozen column normalized concentration and that of the unfrozen control column was expressed as the percent normalized reduction in concentration. Thus

$$\text{Normalized Reduction in Conc. } (\%) = 100(C_{tBH} - C_{fBH})/C_{tmean} \tag{7}$$

where C_{tBH} is the average bottom-half (0–6 cm) control column concentration, C_{fBH} is the average bottom-half (0–6 cm) frozen columns concentration, and C_{tmean} is given by Equation 5. The calculated values for the normalized reduction in concentration for the explosive contaminants are given in Table 1.

Analogous analysis performed for the explosive contaminants with Equations 1–7 was done for the VOCs. The unfrozen control column A data was used to replace column E in the above equations. The frozen columns B, C and D replace columns F, G and H. Calculated values for soil profile concentrations for the VOCs are shown in Table 2.

The second analytical method used to test experimental hypothesis compares, using the Student t statistical significance test (Bauer [10]; Draper and Smith [11)], the regression slope of the concentration profile for the

Table 1. Approximate changes in explosive contaminant concentration in Lebanon silt presumably induced during freezing.* (Approximate freezing front location = 6 cm from bottom end.)

TYPE OF CONTAMINANT	DISTANCE FROM SAMPLE BOTTOM (cm)	UNFROZEN CONTROL SAMPLE CONC. (C_t)	NORM. AVG. CONTROL SAMPLE CONC. (C_t/C_{tmean})	AVG. FROZEN SAMPLE CONC. (C_f)	NORM. AVG. FROZEN SAMPLE CONC. (C_f/C_{tmean})	NORM.* REDUCTION IN CONC. $(C_t-C_f)/C_{tmean}$ (%)
HMX	Bottom-Half (0-6 cm.)	2.30	0.95	2.51	1.04	-8.81
RDX	Bottom-Half (0-6 cm.)	0.77	1.02	0.71	0.94	8.28
TNT	Bottom-Half (0-6 cm.)	4.71	1.07	4.34	0.99	8.40
2,6-DNT	Bottom-Half (0-6 cm.)	5.86	1.05	4.96	0.89	16.10
O-NT	Bottom-Half (0-6 cm.)	3.21	1.07	2.00	0.67	40.36
M-NT	Bottom-Half (0-6 cm.)	4.04	1.08	2.65	0.71	37.19

* Calculated concentration changes were obtained by dividing each column into two equal segments, and by averaging concentration profile over the bottom frozen half segment.

Table 2. Approximate changes in volatile organic concentration in Lebanon silt presumably induced during freezing.* (Approximate freezing front location = 6 cm from bottom end.)

TYPE OF CONTAMINANT	DISTANCE FROM SAMPLE BOTTOM (cm)	UNFROZEN CONTROL SAMPLE CONC. (C_t)	NORM. AVG. CONTROL SAMPLE CONC. (C_t/C_{tmean})	AVG. FROZEN SAMPLE CONC. (C_f)	NORM. AVG. FROZEN SAMPLE CONC. (C_f/C_{tmean})	NORM.* REDUCTION IN CONC. $(C_t-C_f)/C_{tmean}$ (%)
CHLOROFORM	Bottom-Half (0-6 cm.)	64.05	0.96	48.83	0.73	22.83
TOLUENE	Bottom-Half (0-6 cm.)	9.10	1.12	7.36	0.91	21.40

* Calculated concentration changes were obtained by dividing each column into two equal segments, and by averaging concentration profile over the bottom frozen half segment.

unfrozen control column with that of the average concentration profile for the three frozen columns for each analyte. All the data for the three replicate frozen columns were combined and used to least-squares fit the combined 78 data points for the frozen slope estimate. Duplicate values at each location were used for the control column.

For each analyte, a value of t was calculated based on the slope comparison analysis, and the significance level of the difference between the slopes was obtained from the Student t table. A significance level less than 95% was considered insignificant for any difference between the slopes to be considered substantial for the control and frozen sets of data. And a probability level of equal to or more than 95% was considered significant. Also, an F-test was used to check if the intercept of the regression line equation is different from zero before the Student t statistical comparison analysis was performed. The results of the comparison between the regression slopes for the frozen and control concentration profiles are summarized in Table 3.

Table 3. Comparison between the regression slopes of contaminant concentration profiles for control and combined frozen silty soil columns using t-test significance analysis.

TYPE OF CONTAMINANT	CONTROL SLOPE	COMBINED FROZEN SLOPE	t-TEST SIGNIF. LEVEL	OCTANOL-WATER PARTITION COEFFICIENT (K_{OW})*	GENERAL COMMENT
	-----µg/g per cm----		(%)		
HMX	3.25E-03	-9.55E-02	86.5	1.36	NS; < 95%
RDX	-3.58E-03	-6.89E-03	41.0	7.59	NS; < 95%
TNT	-1.02E-01	-5.60E-02	82.0	67.6	NS; < 95%
2,6-DNT	-8.92E-02	-2.99E-02	76.0	97.0	NS; < 95%
MNT	-1.07E-01	-6.70E-03	97.5	263.0	S; > 95%
ONT	-7.85E-02	-1.17E-03	96.5	199.5	S; > 95%
CHLOROFORM	4.77E-01	2.38E+00	74.0	93.3	NS; < 95%
TOLUENE	-1.82E-01	-9.58E-02	35.0	490.0	NS; < 95%

S = Statistically Significant Difference Between Slopes

NS = No Statistically Significant Difference Between Slopes

* Values obtained from Hansch and Leo (12), Leggett (13) and Jenkins (14)

Discussion

Figure 7 shows a composite of the soil moisture content profiles for unfrozen control sample and the three replicate frozen samples used as triplicates involving the explosive contaminants. The main purpose of using triplicate samples is to diminish the effect of several variabilities inherent and usually encountered in a complex nonhomogeneous system such as soil. The moisture profiles for these four samples appeared to agree very well within the measurement accuracy. Similarly good agreement between the unfrozen and frozen sample moisture profiles can be observed for the VOC contaminated soil columns (Fig. 8).

The comparison between the normalized HMX contaminant concentration profile for the unfrozen control soil condition and that for the partially frozen soil condition is shown in Figure 9. The observed anomaly in the control

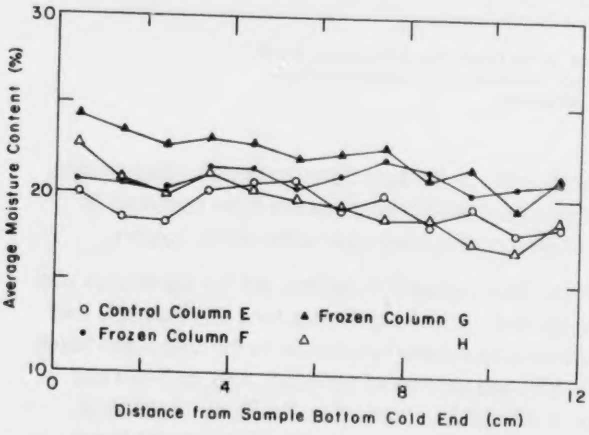

Figure 7. Moisture content profiles of soil columns with explosives.

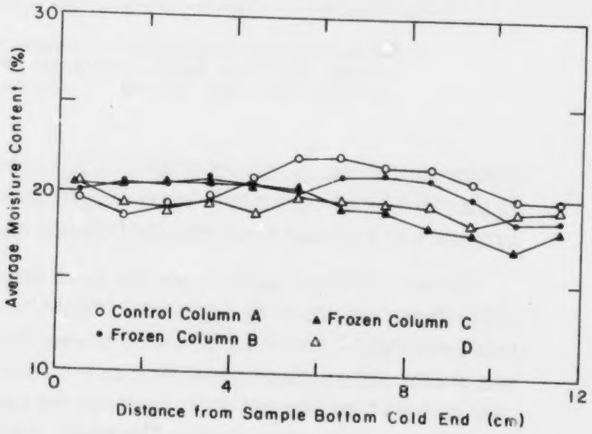

Figure 8. Moisture content profiles of soil columns with VOCs.

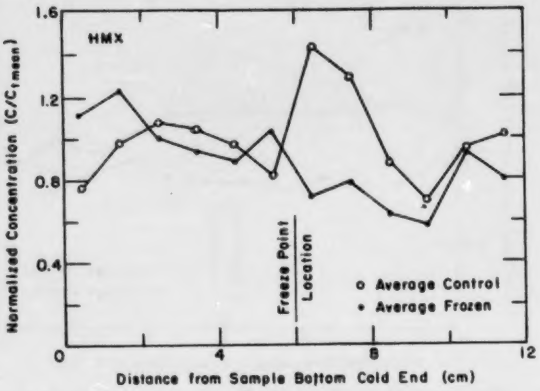

Figure 9. Normalized HMX concentration profiles in Lebanon silt.

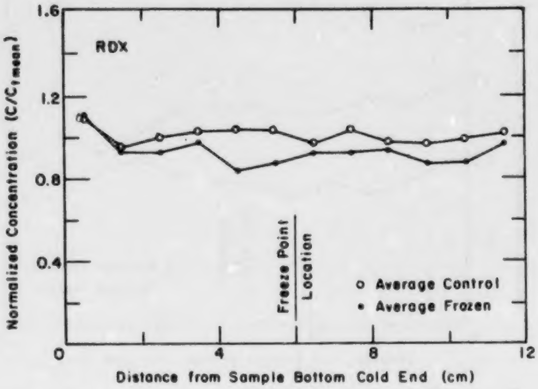

Figure 10. Normalized RDX concentration profiles in Lebanon silt.

concentration profile around the top mid-portion of the sample height was supported by the high values in the sample standard deviation (STD) and coefficients of variation (CV) at these locations.

Very little data scatter was observed for the RDX concentration profiles both for the control and frozen samples, as shown in Figure 10. Moreover, the extreme low STD and CV values for the control sample and the corresponding moderate values for the frozen sample supported this observation. The slight or absent freezing-induced mobility may be due, in part, to the relatively low initial concentration level used. Hence, it was inferred from the data that one freeze cycle at a rate of 0.5 cm/day would not significantly move RDX analyte with an initial average concentration of about 0.76 µg/g.

Concentration profiles for TNT and 2,6-DNT are depicted in Figures 11 and 12, respectively. Very little data scatter along the sample height for control and frozen sample profiles could be observed for both TNT and 2,6-DNT as shown in their respective low STD and CV values. There appeared to be no significant difference in the control and frozen sample concentration profiles for TNT, since its normalized concentration reduction within the frozen portion was about 8%. The concentration reduction for 2,6-DNT was about 16%, indicating no appreciable movement caused by freezing. Comparison of the regression slopes between control and frozen samples for both TNT and 2,6-DNT showed that there was no statistically significant difference between the slopes.

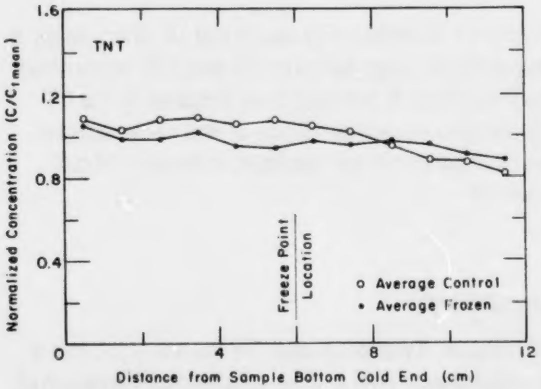

Figure 11. Normalized TNT concentration profiles in Lebanon silt.

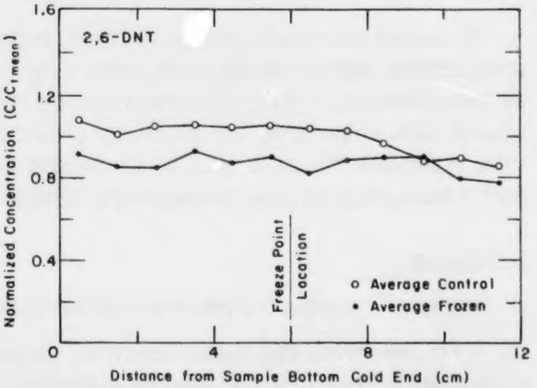

Figure 12. Normalized 2,6-DNT concentration profiles in Lebanon silt.

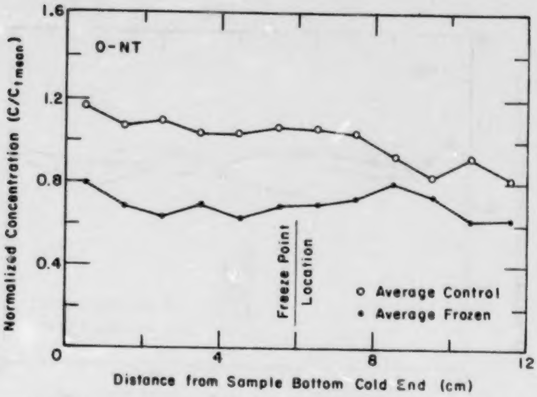

Figure 13. Normalized O-NT concentration profiles in Lebanon silt.

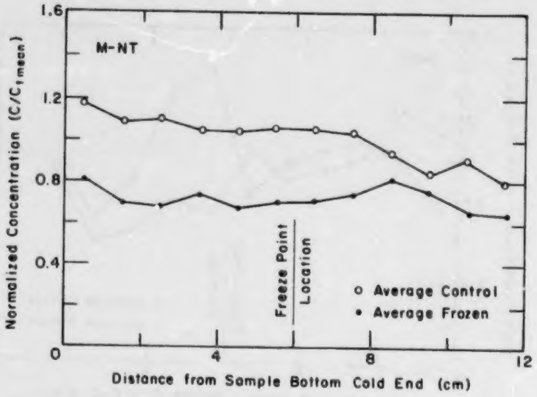

Figure 14. Normalized M-NT concentration profiles in Lebanon silt.

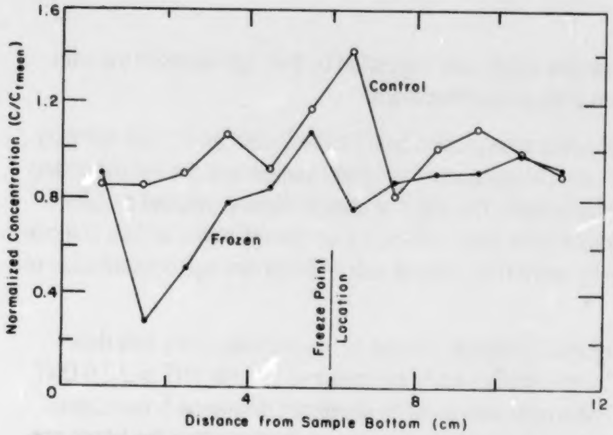

Figure 15. Normalized chloroform concentration profiles in Lebanon silt.

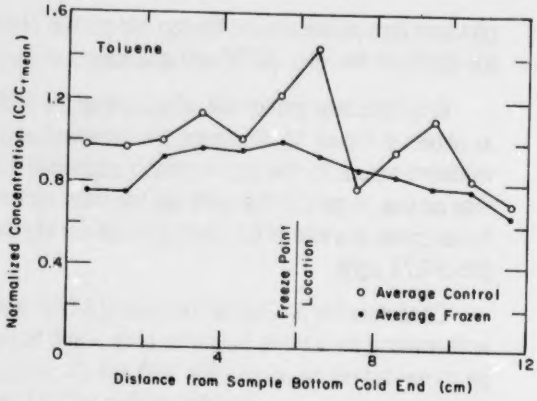

Figure 16. Normalized toluene concentration profiles in Lebanon silt.

Figures 13 and 14 compare the concentration profiles between the control and frozen samples for O-NT and M-NT, respectively. The normalized concentration reductions within the frozen portion behind the freeze front between the control and frozen samples were about 40% for O-NT and about 37% for M-NT.

Normalized concentration profiles for chloroform and toluene are depicted in Figures 15 and 16. Sharp peaks at some locations indicated the large data scatter along the sample height. Large values for CV and STD represented the large differences in the duplicate measurements at different locations. At some locations indicated by the CV value of 100% for the control soil column, one of the duplicate samples was either missing or was below detection limits. In particular, the use of HPLC for the chemical analysis of chloroform in soil was found to be very difficult. Such a technique is still under development at CRREL (Jenkins [7]).

Conclusions

The following conclusions were drawn from this experimental study:

1. For given freeze rate, freeze-thaw cycles, soil and soil moisture, it was postulated that the ability to move a contaminant by freezing strongly depends on the type, initial concentration level and the soil/chemical interaction of the contaminant. Also the ability to easily detect each contaminant in the soil affects how to assess whether or not freezing moves a given type of contaminant.

2. Among the explosives, O-NT and M-NT analytes were significantly reduced by freezing.

3. By comparing frozen and control columns, movement of HMX, RDX, TNT and 2,6-DNT attributed to freezing was statistically insignificant for the relative low concentration used under the freezing condition of one freeze cycle with 0.5-cm/day freeze rate.

4. The inherent volatility of VOCs, the soil spatial variability and the complex chemical interaction (i.e. absorption) between the organic compounds and the soil particles represent some of the sampling problems encountered in the use of artificial freezing as a potential soil decontamination method.

5. Even though there was a distinct difference in the slopes of the concentration profiles for control (unfrozen) and frozen soil columns contaminated with chloroform and toluene, the data in this experiment showed no statistically significant movement induced by freezing at a freeze rate of 0.5 cm/day and one cycle of freezing.

6. An insignificant freezing-induced reduction in concentration (< 10%) was observed for RDX, HMX and TNT. Relatively greater reduction (20–40% change) was observed for 2,6 DNT, O-NT, M-NT, toluene and chloroform.

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ENHANCING LIQUID-LIQUID AND SOLID-LIQUID PHASE SEPARATION BY INTEGRATING ALTERNATING CURRENT ELECTROCOAGULATORS WITH PROCESSING AND WASTEWATER CONTROL SYSTEMS

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ABSTRACT

Coal, pigments, pharmaceutical solids, ceramics, carbon, clays, metallic powders and ores are among the categorical groups of products which are wasted as suspended solids in aqueous-based wash solutions. Phase separation and recovery of these solids by conventional dewatering systems is costly and relatively inefficient. Alternating current can be used to neutralize the electrical charge on fine and ultra-fine particles in aqueous suspensions, and facilitate agglomeration and settling of these particulates without using chemicals while improving recovery efficiencies. The AC electrocoagulator has demonstrated the phase separation of emulsified oils and sub micron particles, thereby purifying water while improving the performance of conventional wastewater control systems. Applications for the removal of soluble pollutants are being investigated.

This paper provides an overview of the technology and discusses applications and benefits in the areas of in-plant processing, industrial wastewater treatment, site remediation and water purification.

INTRODUCTION

In our industrial society, there is an ever increasing awareness of the adverse impacts of inorganic and organic chemicals on the quality of water. Human health and environmental concerns dictate process improvements, substitutes and control systems effective in preventing and minimizing related risks. Wastewaters are of prime concern and warrant reassessment in terms of both volume reduction and pollutant removal. Research must continue to search for effective and efficient solutions to contamination resulting from specific industrial sources as well as contamination related to groundwater and surface run-off.

Advancements in analytical chemistry permit scientists to detect and quantify hazardous chemicals at extremely low concentrations in aqueous media. This capability is expected to support new and stricter regulatory standards which take into account the cumulative impacts of chemical exposure, as well as the potential for chemical transport and transformation.

Wastewater treatment technologies are required to provide optimum removal of suspended and soluble pollutants. Technical strategies emphasizing the reduction of pollution before wastewater generation have been adopted in an attempt to achieve these higher performance levels. These strategies include the separation of fine, and ultra-fine solid products which were previously wasted in waterwash operations. These solid products may be suspended, emulsified and/or partially solubilized in aqueous media to an extent that could be deemed significant in terms of potential hazard and toxic impact. Most of these washwaters require chemical addition to enhance solid agglomeration and settling before conventional mechanical dewatering systems can be employed. Unfortunately, the addition of these chemicals add to the volume of waste generated.

As an alternative to chemical conditioning and flocculation, recent developments indicate that liquid-liquid and solid-liquid phase separation can be achieved using alternating current electrocoagulation (AC/EC). The AC electrocoagulator has been used to flocculate and settle fine solids without the use of chemical aids (1,2,3,4). Recent pilot-scale data (5) demonstrated phase separation of wastewater containing suspended and emulsified oils, thus minimizing potentially toxic pollutants. AC/EC may be easily integrated with conventional process and control systems to enhance solid product recovery and water purification. Waste reduction goals may be accomplished by integrating this technology with a variety of operations which generate contaminated water.

This paper discusses the theory of electrocoagulation with alternating current. Operating variables are reviewed and potential advantages and benefits are highlighted. The current stage of development and plans for future research are discussed in light of applications dealing with water purification, wastewater treatment and site remediation.

STATEMENT OF PROBLEM

Contaminants influence the physical, chemical and electrical properties of water. These properties, in turn, are used to identify environmental concerns requiring control to ensure regulatory compliance. Water is used as a universal "solvent" and its properties vary as a function of use. Solid products subjected to water wash operations create suspensions of finely divided colloidal matter in aqueous media. These wastewaters are generally difficult to phase separate and the suspended solids contribute to the loadings of inorganic and organic pollutants soluble in the aqueous matrix.

Regardless of origin, waste water may also contain the various forms of colloidal matter summarized below:

- solid particles in the form of colloidals with a maldistribution of electrons which are in magnetic suspension in the water media.
- solution components present as water soluble fractions and suspensions due to magnetic forces.
- chemically stable and soluble "salts" displaying an intermediate stable existence in the form of colloidal suspensions of unstable matter.
- suspended inert matter that is colloidal as well as susceptible to precipitation.

Molecular hydrogen bonding is also a consideration. It has a major impact on the "bridging" effect between the water and solid molecules of aqueous sludge. The mechanisms influencing the water associated with solid particles can be summarized as follows:

- o interior adsorption
- o surface adsorbtion
- o capillary absorption
- o interparticle absorption, and
- o adhesion water.

Interior and surface adsorption are referred to as "free" water which is usually removed by mechanical techniques. The other three mechanisms require energy intensive techniques such as thermal drying for phase separation.

The presence of an electrical charge on the surface of particles is often a prerequisite to their existence as stable colloids. This surface charge also depends on the properties of the aqueous phase because adsorption or binding of solutes to the surface of the colloids may increase, decrease, or reverse the effective charge on the particle. The adsorption may occur as a result of a variety of binding mechanisms: electrostatic attraction or repulsion, covalent bonding, hydrogen-bond formation, van der Waals' interaction or hydrophobic interaction.

Flocculation and filtration destabilizes suspended colloids by enhancing aggregation or the attachment tendency of these colloids.

BACKGROUND AND RELATED THEORY

Several studies (6,7,8,9) suggest that most solid particles suspended in aqueous media carry electrical charges on their surface. When the particles are larger than atomic or molecular dimensions, they will tend to separate from the aqueous media under gravitational force unless they are stabilized by electrical repulsion or other forces. Such forces can prevent aggregation into larger particle masses or flocs which are more prone to settling. These surface charges may exist as an ionic double layer or a neutralized electric depole, as conceptually depicted in Figure 1.

Generally, the gravitational force on small particles is weaker than the other forces which can act on the particles. Collisions between particles due to Brownian motion often result in aggregates held together by Van der Waals forces and coagulation may occur in the following ways:

- o The particle crystal lattice may contain a net charge resulting from lattice imperfections or substitutions. The net charge is balanced by compensating ions at the surface such as zeolites, monmorillonite and other clay minerals.
- o The particle solids may contain ionizable groups.
- o Specific soluble ions may be absorbed by surface complexes or compounds formed on the particle surface.

PRINCIPLES OF AC ELECTROCOAGULATION

The electrocoagulator process, invented by Moeglich, et.al. (10,11,12) is based on colloidal chemistry principles using AC power and electrophoretic metal hydroxide coagulation. The process employs two main principles:

- **electrostriction**, whereby the suspended particles are stripped of their charges by subjection to alternating current electrical field conditions in a turbulent stream, and
- **electroflocculation**, whereby minute quantities of metal hydroxides are emitted from the electrodes to assist in flocculation of the suspended particles.

The theory of electroflocculation, or metal ion flocculation, is well established. Iron and aluminum ions have been widely used to clarify water. Recently, Parekh, et.al. (3,13), developed a coagulation system involving the use of metal hydroxide and fine particles. They reported that the optimum coagulation of a metal ion/particle system takes place at the iso-electric point of the metal hydroxide precipitate. Jensen(14) suggests that optimum coagulation may not necessarily occur at the exact point of zero charge, since other mechanisms such as bridging are also important.

A better understanding of the mechanisms which underly the operation of AC/EC is expected to result from research initiated by the State University of New York at Buffalo in June, 1989. The current hypothesis for AC/EC operation is summarized as follows:

- Polar molecules adsorbed on the surface of small particles are neutralized by an equivalently charged diffuse layer of ions around the particle. A zero net change results.
- Non-spherical particles have non-uniformly distributed charges (dipoles) and elongated neutralizing charge clouds surrounding them.

- These dipoles come into play when the charge clouds are distorted by external forces or close proximity of other charged particles.
- External forces such as electric fields can: (a) cause dipolar particles to form chains; and (b) unbalance electrostatic forces resulting in dramatic phase changes (coagulation).

- AC electric fields do not cause electrophoretic transport of charged particles, but do induce dipolar chain-linking and may also tend to disrupt the stability of balanced dipolar structures.

PROCESS DESCRIPTION

INTRODUCTION

AC/EC system designs will vary depending on the characteristics and quantity of waste or process steams being treated, treatment objectives and location. Characteristics, such as particle size, conductivity, pH and chemical constituent concentrations, dictate operating parameters of the coagulator. The quantity and flow rate of the raw solution will effect total system sizing, coagulator retention time, and mode of operation (recycle, batch or continuous). Treatment objectives will establish the type of gravity separation system to use, establish recovery criteria, identify the utility of side stream treatment, define effluent standards to be met and determine the advantages of recycle or multiple staging. Treatment objectives may include product recovery or simply preconditioning prior to using an existing process or as a polishing step after treatment. Location will impact design by imposing physical size constraints and pumping requirements. In-plant industrial applications, for example, may be configured differently than a mobile on-site system used for remediation or treatment of ponded water.

BASIC PROCESS

A basic process flow diagram for AC/EC is presented in Figure 2. Coagulation and flocculation occur simultaneously within the coagulator and in the product separation step. The redistribution of charges and onset of coagulation occur within the coagulator as a result of exposure to the electric field and catalytic precipitation of aluminum from the plate electrodes. This reaction is usually completed within 30 seconds for most aqueous suspensions. The solution may be transferred by gravity flow to the product separation step.

Product separation may be accomplished in conventional gravity separation and decant vessels. Coagulation and flocculation continue in this step until the desired degree of phase separation is achieved. Generally, the rate of separation is faster than methods which employ chemical flocculants or polyelectrolytes, and for some applications the solid phase is denser than the solids resulting from chemical treatment. A recent feasability study (15) demonstrated 95 to 99.5 percent recovery of submicron fines from a 0.6 percent stable suspension after 1.5 hours settling time. Alternative treatment achieved only 80 percent removal after 1.5 hours.

In many applications, the electrocoagulator retention time may be reduced and performance improved by agitating the solution as it passes through the electric field. This turbulence can be induced by using a static aerator concept or simply diffusing small bubbles of air or nitrogen through the solution in the space between the plates. Air has been used in full scale applications treating pond waters and removing fines from coal washwaters. Bottled nitrogen and bottled air have been used in the laboratory to conduct treatability tests. Since the gas used to create turbulence may also strip volatile organics, it is necessary to analyze the vent gas stream, especially when treating hazardous wastes. When appropriate, the vent gases may be collected and treated using available conventional technologies and thus control air emissions within acceptable limits.

After the product separation step, each phase (oil, water, solid) is removed for reuse, recycle, further treatment or disposal. A typical hazardous waste decontamination application, for example, would result in a water phase which could be discharged directly to a stream or to a local wastewater treatment plant for further treatment. The solid phase, after dewatering, would be shipped off-site for disposal, the dewatering filtrate being recycled. Any floatable material would be reclaimed, re-refined, or otherwise recycled or disposed.

OPERATING REQUIREMENTS

The AC/EC operates on low voltage, generally below 110 VAC. It is designed to work at atmospheric pressure, and is vented to alleviate any problems with gas accumulation. As previously mentioned, air abatement apparatus may be added, if necessary.

The internal geometry allows for free passage of particles less than 1/4 inch. While normal operation is relatively maintenance free, some problems can be encountered if process upsets allow heavy particulates to inadvertantly enter the lines. In this case, material build-up could restrict passage and thus retard flow. No permanent damage has been experienced in these cases and the problem has always been alleviated by reverse flushing or minor disassembly and cleanout.

While there has been some question regarding electrode deterioration, in practice none of consequence has been noted. Minor etching occurs on the electrode skins. As nearly as can be theorized, the alternating current cyclic energization retards the normal mechanisms of electrode attack that are experienced in DC systems and reasonable electrode life has been proven. Electrodes were replaced after four months of continuous operation (20 hours per day) in a 250 gpm commercial unit.

Electrical energy costs vary based on the solution being treated and the specific application. Commercial units have treated coal wash waters for $0.40 per 1,000 gallons at power costs of $0.05 per kwH. This cost is more than offset by savings in the chemical costs associated with alternative methods which require the use of polyelectrolytes and chemicals to adjust pH.

RESIDUAL EFFECTIVENESS

Bench-scale tests (15) and full scale field applications (2) have demonstrated a phenomenon referred to as residual effectiveness. Once the solution has passed through the coagulator and settling is complete in the product separation stage, the separated products can be remixed and subsequent phase separation will recur without further treatment through the electrocoagulator. It appears as if the charge redistribution and coagulating forces remain effective for extended periods of time. This phenomenon is important in that mixing and pumping can be accommodated after coagulation, if so dictated by other system design conditions, without losing the phase separation effectiveness. This also indicates that in some applications only a portion of the total contaminated solution would need to be treated. For example, in removing constituents from a pond, a portion of the solution may be treated and returned to the pond until the desired phase separation results. Phase separations have been accomplished by passing as little as 25 percent of the total volume through the electrocoagulator.

EFFECTS AND APPLICATIONS

Studies suggest that alternating current coagulation causes the following effects on the resulting by-products:

- o the magnetic forces associated with liquid suspensions are destroyed.
- o sludges tend to dewater and densify, suggesting a disruption and/or destruction of the hydrogen bonding of water molecules.
- o electronic or ion exchange creates an electro-chemical environment, causing various reactions dependent on contaminating constituents.
- o oils, soap, detergents and cellulosic material can be phase separated from water.
- o inert clay colloidals can be removed from aqueous media.
- o the generation of OH^- as well as the potential for O_2, H_2, O_3 and H_2O_2 may influence soluble pollutants by chemical oxidation.
- o soluble oils phase separated from aqueous media can extract other toxic constituents which are preferentially soluble in the oil fraction.
- o water characteristics created by electrocoagulation and subsequent clarification result in a long lasting demagnetized effluent that resists contamination.

The following advantages were identified as a result of using AC/EC in the coal industry:

- o improved fine coal recovery.
- o improved dewatering rates.
- o reduced filtration time.
- o reduced recirculation of coal and clay fines in closed loop water.
- o reduced buildup of fines and clays on dewatering screens.
- o neutralization of plant water pH.
- o removal of heavy metal and organic carbon from water.
- o reduced plant maintenance.
- o increased plant availability.
- o increased coal yields without sacrificing quality.
- o increased quality at the same or increased yield.
- o reduced freezing of treated coal.

Test data such as presented in Table 1 and 2 support the cited advantages, as well as many of the pertinent principles of the technology.

SUMMARY

The use of alternating current electrocoagulation to break emulsions and phase separate aqueous solutions has been successfully demonstrated without using chemical aids. Based on pilot-scale results and an assessment of potential physico-chemical reactions, the applicability of this technology to various industrial and hazardous waste management applications has been identified. Research activities are underway and/or planned to further investigate this technology and to better define applications and benefits. On-going field demonstrations and treatability studies of emulsions, slurries and suspensions from various industries as well as hazardous waste sites contribute to understanding effective operating parameters. Cost effectiveness is derived from the reduction or elimination of chemical aids, performance improvement of conventional mechanical separation systems, and an overall reduction in the quantity of wastes generated. Applications can be found within almost every industrial sector for a wide range of wastes and in-plant processes.

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TABLE 1 APPLICATIONS OF ELECTROCOAGULATION

APPLICATION	RESULTS	Reference
1. Particulate removal		
a. Water from contaminated soil wash	>washwater clean enough to recycle to the ground	17
b. Clay colloids in ponded water	>99% removal of suspended solids	1
c. Removal of coal fines	improved performance without chemicals	1 - 18
d. Micron size particulates	99 - 99.5% recovery	15
2. Removal of soluble organics		
a. Ponded water	>99% removal of TOC*	1
b. Creosote suspension	>98% removal of TOC	5
c. Emulsion of rolling coolant and waste oils	>90% removal of TOC	5
d. Lake water (DC electro-coagulation)	>95% removal ot TOC	9
3. Metals		
a. Ponded water	>99% removal of Fe, Mn,Al	1
b. Acid mine wastes	>98% removal of Fe,Cu, Al	19
4. Enhanced dewatering		
a. Coal fines	>dewatering rate increased by 30 - 50%	1 - 2

* TOC = total organic carbon

TABLE 2 FIELD TEST RESULTS
ELECTROCOAGULATION OF PONDED WATER

	POND A		POND B	
Parameter	Raw Water	After Treatment	Raw Water	After Treatment
pH	6.4	7.7	7.3	8.3
Suspended Solids	197 ppm	1 ppm	195,000 ppm	15 ppm
Dissolved Solids	—	—	7,212 ppm	3,344 ppm
Soluble Iron	88 ppm	0.13 ppm	—	—
Total Iron	285 ppm	263 ppm (in sludge)	3,500 ppm	0.18 ppm
Manganese	3 ppm	1.9 ppm	104 ppm	0.02 ppm
Aluminum	—	—	304 ppm	0.08 ppm
Alkalinity	—	—	48,500 ppm	400 ppm
TOC	—	—	11,000 ppm	30 ppm

Adapted from Plantes, Reference [1]

FIGURE 1

SURFACE CHARGE DISTRIBUTIONS

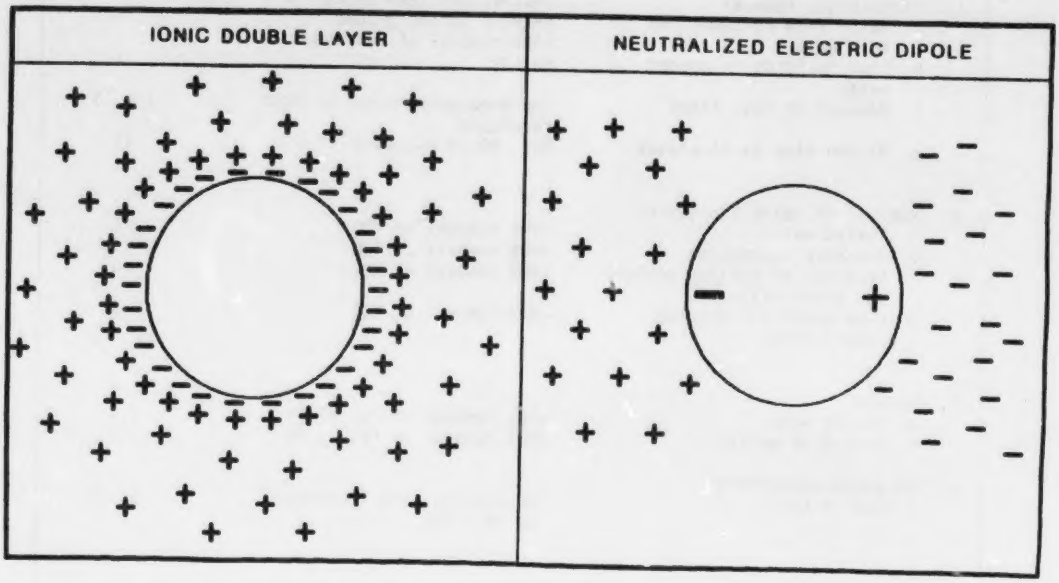
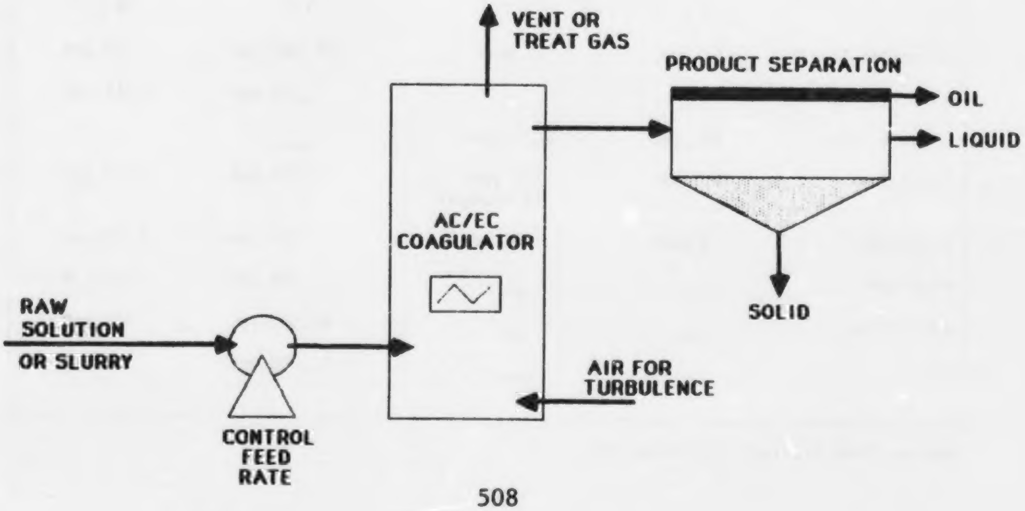

IONIC DOUBLE LAYER
NEUTRALIZED ELECTRIC DIPOLE

FIGURE 2

AC/EC PROCESS FLOW DIAGRAM


VENT OR
TREAT GAS
PRODUCT SEPARATION
OIL
LIQUID
AC/EC
COAGULATOR
SOLID
RAW
SOLUTION
OR SLURRY
AIR FOR
TURBULENCE
CONTROL
FEED
RATE

Machine Coolant Maintenance Leading to Waste Reduction

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ABSTRACT

The volume of machine coolant waste can be reduced through maintenance. Coolants are generally considered a waste due to rancidity, not due to a loss of their cooling properties.

Through a grant study and intern projects administered by MnTAP the steps for maintaining coolants and the means to implement them were uncovered. Maintenance involves the removal of tramp oils from the machine's coolant sump, control of bacterial growth in the coolant and maintenance of the proper coolant to water ratio.

INTRODUCTION

There are approximately 14,000 companies performing machining operations in the United States, generating sales of $20 billion per year. Machine shops make parts from metal stock for a wide variety of industrial products, using processes such as drilling, turning, lapping, grinding, and broaching. Machine tools used in these operations are cooled by fluids, generally referred to as "coolants", in order to extend tool life and enhance product quality. When these coolants reach the end of their useful life, their disposal may be regulated as a hazardous waste in some states.

Spent coolants may contain contaminants which can pollute groundwater, surface waters, and upset wastewater treatment plant (WWTP) operations. These contaminants may include tramp oils, high levels of biocides, heavy metals and nitrates. In addition, they are generally a high strength waste as measured in biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total suspended solids (TSS). Preliminary studies on the treatability of coolants indicate that the material is biodegradable if sufficient acclimation time is provided (acclimation time is the length of time between the addition of a substance and a noticeable change in the oxygen uptake by the organisms). It should be noted that these results are believed to be plant specific and the acclimation time will vary depending on the exposure to high strength industrial waste the organisms have received in the past. In addition, the acclimation time may exceed the detention time of the WWTP and result in the material passing through the WWTP into the receiving water.

The Minnesota Technical Assistance Program (MnTAP) became involved with this wastestream when a number of generators called regarding proper coolant management and disposal. A company approached MnTAP in 1986 for an intern to help them establish an acceptable management strategy for their coolant waste.

The early part of the intern project focused on treatment methods (chemical splitting technologies) which would break the emulsion for each of the two brands of coolants the company used. Treatment would generally result in the water portion being sewered and the coolant/oil portion recycled through used oil haulers. After repeated efforts at treatment it was determined that the ability to split the coolant emulsion by chemical treatment was coolant specific and therefore not broadly applicable.

During this project, information about coolant maintenance as a means to reduce the volume of waste generated was also emerging. Since the factors affecting coolant life were not coolant specific, the steps required for coolant maintenance and implementation were identified as areas which needed to be further explored.

PURPOSE

MnTAP wanted shop based data which would indicate the steps required to accomplish maintenance and show how they could be implemented. The literature indicated that coolant life could be prolonged by removing the tramp oil which accumulates in the machine's coolant sump, controlling the bacterial growth in the coolant and maintaining the proper coolant to water ratio. Two opportunities were presented to MnTAP to test these principles in a shop setting. Washington Scientific Inc. conducted a year long grant study which was administered by MnTAP, and Midwest Electric Products was selected as a company for a 1988 MnTAP intern project. The details of these projects and their results are outlined in the next section.

APPROACH AND RESULTS

It is important to note that both companies listed above approached the projects with the following elements in mind:

1) Starting with the lowest cost techniques and expanding them as needed.
2) Examining the site specific problems of implementation and modifying the operations if feasible where needed.
3) Starting with simplest (or easiest) equipment to operate.

Washington Scientific Industries, Inc.

Background

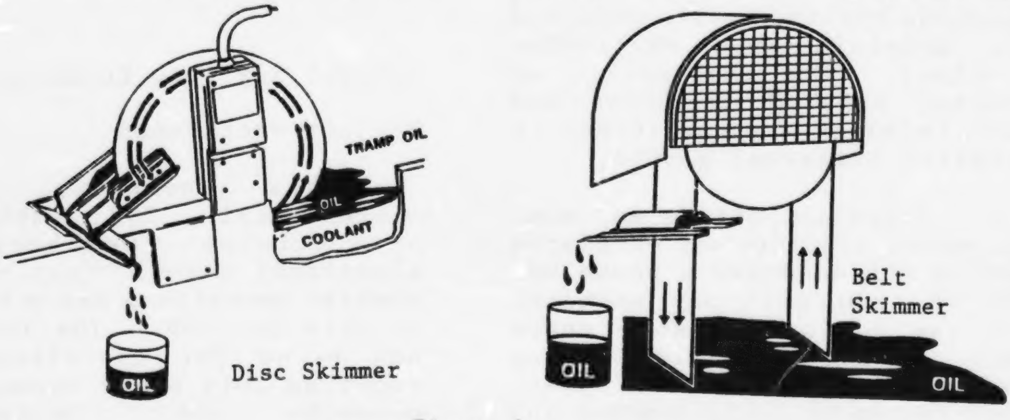
This machine shop has approximately 150 employees doing precision machining and assembly of motors and drives for the computer industry and other specification manufacturers. A wide variety of machine tools are used which have in the past generated as much as 120 55-gallon drums per year of waste water-soluble coolant.

The research project was designed to study the effects of maintenance practices and coolant type on coolant life. Baselines were established for coolant maintenance practice, coolant life, and tool performance. Coolant life was found to be as short as two weeks in some machine sumps, due to the formation of hydrogen sulfide by anaerobic bacteria and, in some cases, reduced tool performance. Maintenance involved coolant removal and sump cleaning as required because of excessive hydrogen sulfide odor. A specific water-soluble coolant which does not require the labor and expense of biocide additions for bacterial control was substituted for the coolants used in all operations except grinding and magnesium machining. The performance of this coolant was evaluated throughout the project for tool performance, resistance to bacterial contamination, and health effects on operators.

Development and Implementation

It took several months to characterize current practice and coolant performance. Oil skimmers, a centrifuge, and coolant changing/coolant sump cleaning practices were evaluated for oil removal efficiency and effect on coolant life. Use of the mobile centrifuge was tested by cleaning the coolant in the sumps of a group of 25 machines. It was found that this is the maximum size group for one person to maintain, i.e., the first sump required cleaning by the time the 25th was done. Even though the coolant was cleaned adequately, this was judged to be an inefficient use of labor.

At the same time that the centrifuge was being evaluated, disk and belt oil skimmers (see Figure 1) were installed on a



Disc Skimmer

Belt Skimmer

Figure 1

study group of five machines which represented a spectrum of machining operations and raw materials. All machines are a common size, one to four years old, and used on two-four week production runs. Operators, material and processes were held constant as much as possible. The project also evaluated different coolant change procedures for labor requirements and effectiveness. When coolant is changed or cleaned (oil removal, solids removal), it is important to clean the coolant sump to minimize carry over of bacteria and other contamination. The ideal method is to vacuum and clean the sump until all contaminants are removed. However, this can be difficult in practice because of limited sump access. Therefore, the objective of the project was to determine the best combination of effectiveness and efficiency.

Results

The selected coolant, even after being recycled for over seven months, met or exceeded all performance requirements. There was no incidence of dermatitis among the operators. It is important to note that no biocide additions were required to maintain this particular coolant. The combination of normal pumping agitation and oil skimming was sufficient to control bacterial growth.

A coolant change and sump cleaning practice was developed which standardized a procedure to be used with any machine. It was found that some sumps are easier to clean than others, especially when access covers can be fully removed and corners (along bottom and sidewalls) are rounded. It is believed that this change routine, which requires approximately five hours per sump, extends coolant life. However, it was not evaluated in isolation from other changes.

Both disk and belt skimmers effectively reduced coolant oil and grease concentrations. It proved necessary to install timers and pumps to reduce the amount of coolant carried out with the oil, but these were simple changes. It was also necessary to modify several sumps to provide access for the skimming equipment. In some cases, a skimmer was moved from sump to sump; on other machines, the installation was permanent. Both modes of operation were equally effective in extending coolant life.

The results of tests conducted during this project show that it is possible to extend the life of machine oil coolant. Simple skimming of tramp oil using any of several different methods was cost-effective and controlled oil and grease concentrations well.

Midwest Electric Products

Project Background

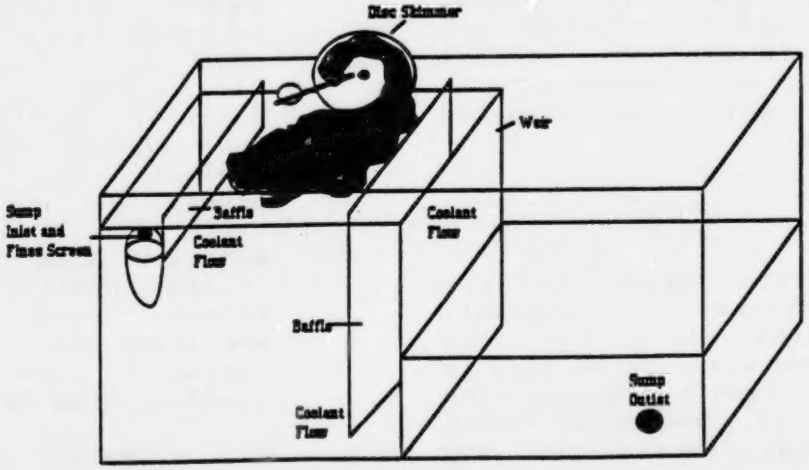
This company, with approximately 250 employees manufactures weatherproof electrical boxes. Many of the machine operations use a water-soluble coolant. The company had asked for assistance in reducing this waste because of concerns over increasing charges for BOD/COD levels, and the uncertainty about the continued acceptance of the wastewater by the city.

The intern project started with a waste survey, in which the sites of waste generation were identified and the waste quantities from each site were measured. There were seven machine sumps generating batch dumps ranging from 10-40 gallons. In most cases machine operators dumped the coolant when it became rancid. The total annual waste coolant was estimated to be about 2000 gallons.

Development and Implementation

At one site in the plant, several machines already were situated close to each other, which made the idea of plumbing their sumps together attractive as that would reduce the time required for maintenance. At the same time that plans were being made to do this, the student conducted tests to evaluate the effectiveness of the methods identified in the literature on prolonging coolant life. While results were not always conclusive, preliminary findings supported the validity of these methods (removal of tramp oil, bacteria control, maintaining proper coolant to water ratio).

Therefore, plans were developed for a central sump, shown in Figure Two, to service the eleven drilling and tapping machines. The system was designed to include periodic oil skimming, removal of metal fines and agitation of coolant once oil skimming was completed. The central sump was fabricated at the company site, starting with a purchased cattle trough for the holding tank. Baffles were welded into the center of the tank so that an oil skimmer could remove the oil at one end of the tank before the coolant flowed over the weir to the other end of



Central Sump

Figure 2

the tank where it is agitated by a pump prior to recirculation to the machines. Agitation was incorporated into the design so as to discourage the growth of anaerobic bacteria. A programmable timer was purchased so that the disc oil skimmer would operate only periodically, thus reducing quantities of coolant removed with the oil. Stainless steel screens were fabricated to collect fines at each worktable. In addition a bag filter placed over the inlet to the central sump also removes metal fines. The cost for the components purchased and the labor needed to install the tank was approximately $800.

While agitation, removal of fines and oil happen automatically in the central sump, pH control and bacteria level require manual monitoring. Strips are used to read pH and also bacterial count weekly. When these parameters register outside the expected operating range, caustic and/or biocide are added. In addition, coolant concentration is monitored with a refractometer, and adjusted as needed.

Results

In late August, the new system became operational. Four months later, the same coolant was still being used in the sump. Weekly, the operator monitors pH, bacterial count and coolant concentration and makes the necessary changes. While this involves some effort on the part of the operator, the bonus is that employees have a more pleasant machining environment as dermatitis is not a problem nor is there a rotten egg smell associated with hydrogen sulfide formation. In addition the wastewater strength has been reduced by discharging less coolant waste. Preliminary results indicate that both the BOD and COD of the total wastewater from the company have been reduced by approximately 50 percent since the centralized sump became operational.

SUMMARY AND CONCLUSIONS

The Department of Energy has estimated that proper maintenance has the potential to reduce the volume of emulsified oil waste by 80 percent. The steps for maintenance for one type of emulsified oil, coolants, are briefly outlined below:

- o Properly designed sumps to give access for skimming/cleaning equipment. Sumps should also be constructed out of material easily cleaned and should allow the coolant to circulate freely.
- o Routine sump cleaning (either chemically or with steam) needs to be performed when coolant is replaced to remove residual sump bacteria.
- o Oil skimming should be performed routinely. The two most practical skimming devices for coolant maintenance are disc and belt skimmers.

Some additional factors to keep in mind when using skimming devices include:

- access to the sump will limit the type of skimmer which can be used
- use of timers to intermittently remove oil and reduce the amount of coolant carried out of the sump.
- placement of skimmers near the sump's pump since the pumping action will draw the tramp oil towards it.
- use of a low speed/ volume pump to reduce the possibility of drawing the tramp oil into the pump.

o Metal chip removal should be performed routinely to minimize the machine fouling and minimizing sites for bacterial growth. Screens can also be used to prevent the chips from entering the system.

o Adjusting the pH of the coolant or addition of a biocide to control bacterial growth.

o Refractometers or coolant proportioners should be used to maintain the proper coolant to water ratio. Both are fairly inexpensive devices.

Although the maintenance steps are not coolant dependent, higher quality coolant did not require the addition of biocides or pH adjustments. In some cases where tooling machines did not have access for maintenance equipment, the higher grade coolant did have a longer life. The maintenance steps were also found to be more streamlined by using a single coolant in the shop.

At some point waste coolant will still need to be treated for disposal. A number of treatment technologies exist including: high speed centrifuges, chemical splitting processes, ultrafiltration, coalescing and reverse osmosis. These technologies require further research to determine their performance.

Field work and other research directed by our office has shown that the volume of machine coolant generated as waste can be reduced by implementation of relatively simple technologies and techniques. Factors important to successful implementation include a limited number of coolants, tolerance of selected coolant to a wide variety of conditions, and careful solution and equipment maintenance.

Barriers to implementation include lack of a willingness to change established processes, limited availability of shop-based testing data, and initial capital costs, especially machine tool modifications. As treatment and disposal costs continue to rise, more attention will be given towards waste minimization.

ACKNOWLEDGEMENTS

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MnTAP was established at the University of Minnesota in 1984 as a non-profit, non-regulatory program through a grant from the Minnesota Pollution Control Agency. MnTAP's goals are to assist Minnesota businesses with waste management and waste reduction. Assistance is provided through telephone consultations, on-site visits, student internships, the gathering of technical information and acting as a clearinghouse.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

WASTE GYPSUM - ITS UTILIZATION AND ENVIRONMENTAL IMPACTS

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ABSTRACT

Waste gypsum (WG), also referred to as phosphogypsum - the main by-product of the wet process of phosphoric acid manufacture - is amongst the most significant wastes generated by the chemical industry of Poland. Up till now most of these waste materials have been disposed of to landfills without taking any conventional safety measures. It resulted in a serious pollution of soil and groundwater in the vicinity of WG landfills.

WG from apatite processing (from Kola Peninsula, SU) contains significant amounts of valuable and recoverable rare elements as yttrium and lanthanide series (Y+LS). The total amount of these elements in one of the WG landfills approaches 9200 tons.
A joint concept of Y+LS recovery and production of building gypsum has been developed. Presented are also the results of pilot studies.

INTRODUCTION

Existing and abandoned industrial landfills create serious hazards to the environment. In Poland, most of them fail to be properly located; they meet neither legislative regulations nor environmental requirements. Many kinds of wastes are actually suitable for reuse in the industry, directly or after appropriate treatment.

Among them is also WG generated during the manufacture of wet phosphoric acid.
WG landfills in Poland cover a total area of dozen hectares

and are noxious to their vicinity because of dust emissions. acidic leachates and runoff.

Systematic stripping of the landfills. processing and reuse of the deposited waste material are very important from both economical and ecological viewpoints. As a result. Polish industry obtains fresh starting materials. and the landfills receive considerably lower quantities of hazardous wastes. Needless to say that these lead to a significant abatement of environmental pollution in general. and in the immediate vicinity of the landfill in particular.

PURPOSE

The purpose of this study can be itemized as follows:

1. Identify main sources of environmental pollution caused by the WG landfill.
2. Evaluate actual level of environmental pollution in the landfill vicinity.
3. Propose proper remedial measures in order to minimize environmental damage.
4. Evaluate total resources of Y+LS in the WG landfill.
5. Propose a concept and conduct a pilot-scale study on Y+LS recovery and on the production of building gypsum.

APPROACH

Cooperation

This study was conducted under cooperation of the following institutions:

Institute of Environment Protection Engineering of the Wrocław Technical University.

Institute of Inorganic Chemistry and Metallurgy of Rare Elements of the Wroclaw Technical University,

Wrocław Geological Enterprise. and

Research Center "Hydro-Mech" of Kowary.

Wastes

Chemical analyses as well as pilot-scale studies on Y+LS recovery were conducted on the waste material from current production of phosphoric acid (calcium sulfate hemihydrate or mixture of hemihydrate and dihydrate) and on the material from the landfill (dihydrate).

Deposited WG was sampled in 13 boreholes at every 0.5 m of landfill depth.

Landfill site

In the time span of 1970 to 1983 the landfill received only WG in the form of dihydrate.

Since 1983. disposal has been carried out in the following manner: hemihydrate or mixtures of hemihydrate and dihydrate have been placed in the higher part of landfill. whereas mixtures of partly dewatered wastewater sludge and sodium fluosilicate sludge removed from a lagoon have been disposed of to the lower part of the landfill.

The WG landfill under study covers an area of ca. 11 hectares. Total volume and weight of deposited WG have been determined as amounting to 1.6 million cubic meters and 2.0 million tons. respectively.

Fig. 1 shows the landfill site and its vicinity.

The landfill subsoil is a glacial outwash aquifer with a thickness of ca. 7 m. It consists of beds and lenses of fine to coarse sand and gravel with thin lenses and beds of fine to medium sand and silt interbedded with the coarser material. The glacial outwash aquifer is underlain by a glacial till.

Groundwater was sampled in 21 monitoring wells located on the landfill foreland. Soil samples have been collected near the monitoring wells.

Procedures

Standard methods were used for examination of groundwater, surface water, runoff, and leachates. Moisture content in WG was determined by drying at temperatures of 50°C or below in order to avoid dehydration and removal of crystallization water from dihydrate. Total Y+LS content was determined by the titration method with Na_2EDTA or by colorimetric analysis, using xylenol orange as indicator.
Atomic absorption was used for the examination of particular elements.

PROBLEMS ENCOUNTERED

Environmental pollution in the vicinity of the WG landfill accounts only for a part of the overall pollution produced by the chemical plant itself. It was practically impossible to exactly attribute the environmental damage to respective source having at hand the existing system of environmental monitoring.
According to generalized estimations, release of noxious substances with runoff and leachates as well as with dust blowing from the landfill does not exceed 2% of the total emission from the whole plant.

RESULTS

The results of the chemical examination of WG. as well as of the mixture of sludges are presented in Table 1.
The main component of WG - calcium sulfate dihydrate or a mixture of hemihydrate and dihydrate - approaches for ca. 90 % of dry wt.. The wastes also contain CaF_2. $Ca_3(PO_4)_2$. SiO_2. Na_2SiF_6. H_3PO_4, and H_2SO_4.

Rare elements are the most valuable compounds of the WG. Yttrium - Y and lanthanide series - LS (La. Ce. Pr, Nd. Sm. Eu. Gd. Tb. Dy, Ho. Er. Tm. Yb. Lu) defined as the sum of oxides (Y_2O_3 + LS_2O_3). occur at an average concentration of 0.62 dry wt. %.
Typical concentrations are as follows (in mg/kg of dry wt.) Y, 151; La. 1063; Ce. 2142; Pr, 144; Nd. 887; Sm. 92; Eu. 25; Gd. 86; Tb. 21; Dy, 38; Ho. 12; Er. 15; Tm. 0.8; Yb. 5.4; Lu. not determined. [1].
A special issue is the estimation of the radioactivity level in WG. It is interesting to note that - unlike the gypsum coming from phosphorite processing (Morocco, Florida) - WG which originates from the processing of apatite displays a very low radioactivity, comparable with that of natural

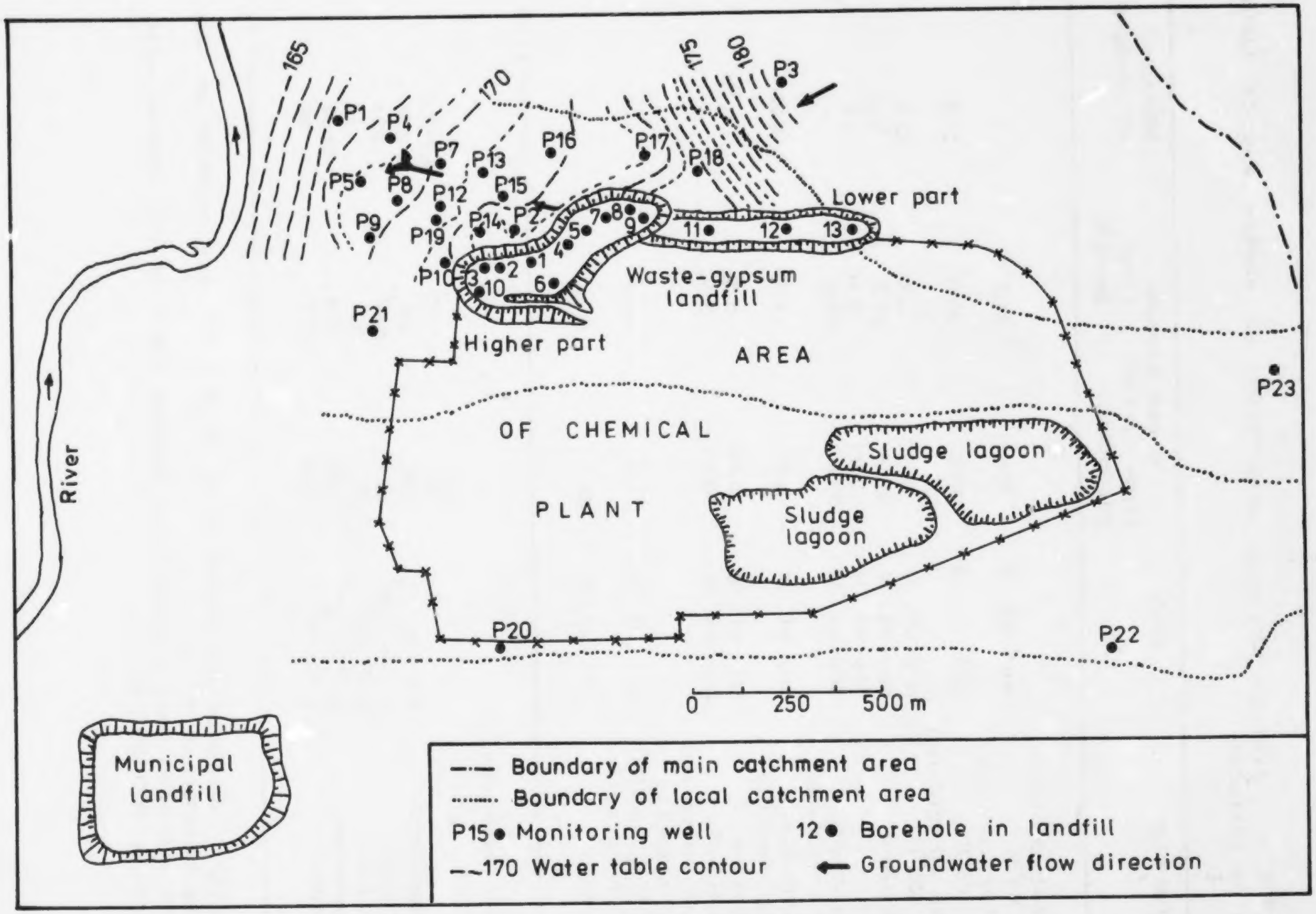

165
170
175
180
P1
P3
P4
P5
P7
P8
P9
P10
P12
P13
P14
P15
P16
P17
P18
P19
P2
P21
P20
P22
P23
1
2
3
4
5
6
7
8
9
10
11
12
13
Lower part
Higher part
Waste-gypsum landfill
AREA
OF CHEMICAL
PLANT
Sludge lagoon
Sludge lagoon
River
Municipal landfill
0
250
500 m
Boundary of main catchment area
Boundary of local catchment area
P15 ● Monitoring well
12 ● Borehole in landfill
170 Water table contour
Groundwater flow direction

Fig.1 Plan of study area

TABLE 1. Average chemical composition of wastes and of their water extracts

Parameter	Unit	Waste gypsum from current production	Waste gypsum from landfill	Mixture of sludges
Water content at 50°C	wet wt. %	20.2	11.2	-
Water content at 105°C	wet wt. %	25.3	23.3	61.2
Loss on ignition at 600°C	dry wt. %	6.6	6.1	12.8
Calcium	dry wt. %	22.5	21.2	9.4
Iron	dry wt. %	0.04	0.10	1.8
Sulfates	dry wt. %	58.8	53.5	-
Water-soluble phosphates, PO_4^{-3}	dry wt. %	1.15	1.39	3.73
Water-soluble fluorides, F^-	dry wt. %	0.08	0.21	0.19
$Y_2O_3+LS_2O_3$	dry wt. %	0.62	0.62	-
Total water holding capacity (Field capacity)	wet wt. %	54.0	40.0	-
Water retention capacity	wet wt. %	28.7	13.8	-
Water extracts				
pH		2.6	1.7-4.7	4.1-5.1
Conductivity	mS/cm	3.8	2.8	2.3
Sulfates	g SO_4^{-2}/m^3	2328	1649	824
Fluorides	g F^-/m^3	57	39	67
Phosphates	g PO_4^{-3}/m^3	860	974	1460
Calcium	g Ca/m^3	800	577	88

REMARKS: All data expressed in % of dry wt. are related to the drying residue at 105°C.
Water extracts were prepared by shaking 100 g of raw wastes with 1 liter of distilled water.

TABLE 2. Radioactivity of WG [3]

WG	Radioactivity, Bq/kg dry wt. ^{40}K	^{216}Ra	^{228}Th
from apatite processing:			
- raw	110	31	11
- after recovery of Y+LS	98	16	16
from phosphorite processing	113	575	19

gypsum. This enables a safe utilization of the recovered gypsum for building purposes (Table 2) [3].

The pH of the waste and of its water extract is strongly acidic. Both acids - phosphoric and sulfuric - are first leached from the wastes deposited on the landfill. This process also occured in the column tests.

The investigations carried out in the vicinity of the landfill have shown that the highest degree of soil contamination is measured immediately at the landfill foot (primarily at the monitoring wells P2, P10, P14 and, also at P12, P16 and P17). Those soils are characterized by increased contents of sulfates, phosphates, fluorides, calcium, and potassium which are the main components of waste gypsum (Table 3). Slope runoff and top dust blowing and deposition have been identified as the main sources of soil contamination in the nearest vicinity (in a radius ca. 80 m) of the landfill.

Groundwater in the landfill vicinity is highly mineralized (in terms of calcium sulfate concentration which, in some samples, approaches the saturation level).
Leachates and excess water from the sludges deposited in the lower part of the landfill (located predominantly in a sand excavation) have been considered as the principal sources of groundwater pollution.
The remaining are as follows: runoff from landfill slopes, roads and neighbouring area as well as leaching of dust deposited on the soil in the landfill vicinity (mainly from the area of the chemical plant).

The highest concentrations of pollutants are found to occur in water samples from the monitoring well P17 (1903-2131 g SO_4^{-2}/m^3, 0.26-2.79 g F^-/m^3, conductivity of 2.63-2.87 mS/cm, pH of 3,92-4.31). Water sampled at the monitoring wells located on the foreland of the higher part of the landfill is characterized by considerably lower concentrations of main pollutants ($0-0.3$ g F^{-}/m^3, $518-1540$ g SO_4^{-2}/m^3, cond. of 1.01-2.32 mS/cm).

Natural, relatively high concentration of calcium sulfate is typical for the groundwater of this area ($224-425$ g SO_4^{-2}/m^3, $95-180$ g Ca/m^3),thus only a part of calcium sulfate can be attributed to the landfill impact. Groundwater also carried Y+LS at total concentrations below 1.0 g/m^3, expressed as Y_2O_3 + LS_2O_3 (Table 3). Because of groundwater pollution, it was necessary to discontinue any use of the farm wells in the radius of ca. 1 km from the landfill either for household or for farming purposes.

The results show that infiltration of rainwater inside the WG (in the higher part of the landfill) is considerably decreased by

TABLE 3. Average composition of groundwater and soil samples collected in the landfill vicinity [1,4]

Monitoring well	pH	Groundwater Sulphates g/m^3	Fluorides g/m^3	Y_2O_3 + LS_2O_3 g/m^3	Soil (mg/kg dry wt.) Sulphates	Fluorides	Y_2O_3 + LS_2O_3
P 1	6.5-7.3	727	0.09	1.10	2800	9	800
P 2	5.6-6.8	1271	0.13	0.48	3000	12.4	1200
P 3	6.5-6.8	1031	0.11	0.51	-	-	400
P 4	6.4-7.2	767	0.13	0.64	-	-	500
P 5	6.1-7.0	216	0.15	1.01	-	-	-
P 7	6.0-6.3	926	0.02	0.59	trace	10	500
P 8	6.3-7.1	845	0.18	0.40	-	-	-
P 9	5.8-6.7	1213	0.10	0.46	3200	15	-
P 10	5.4-5.9	1400	0.06	0.91	4200	28	-
P 12	5.8-7.0	883	0.14	0.47	3300	7.4	600
P 13	5.9-7.1	976	0.17	0.68	-	-	-
P 14	6.2-6.6	855	0.07	0.38	4400	9.7	-
P 15	5.5-6.5	1186	0.10	0.67	-	-	-
P 16	5.7-6.3	1174	0.42	0.91	2900	11.2	-
P 17	3.9-4.3	2022	2.07	0.38	-	12.6	-
P 18	6.0-7.1	1162	0.10	0.46	-	-	900
P 19	4.9-6.5	949	0.07	0.42	-	-	-
P 20	6.6-7.6	525	0.12	0.30	-	3.6	600
P 21	7.3	915	n.d.	-	-	-	-
P 22	6.7	425	n.d.	-	-	-	-
P 23	6.6	224	n.d.	-	-	-	-

n.d. - not detected

(1) hydration of hemihydrate to dihydrate which makes a crust form on the top and on the slopes of the landfill, thus promoting more intensive runoff,

(2) advantageous properties of the compacted material (e.g. low permeability, high water holding capacity (field capacity), and high capillary rise).

Raw hemihydrate has a moisture content of ca. 20 wt.% and water holding capacity amounting to 54 % of the input weight. Apart from the actual moisture, the water holding capacity also comprises hydration ability (maximum crystallization water content of 14 wt.%) and retention capacity of 20 wt.%.

These data indicate that in the area under study the annual total of precipitation (0.656 mm/a) is to be stored in well compacted, homogeneous WG layer of ca. 1.6 m of height (without taking into account water loss due to evaporation and runoff). Total water content of raw WG at its field capacity amounts to ca. 43 wt.%. Material sampled from the boreholes (dihydrate) was characterized by a total water content of 20-33 wt.%. In all of the samples, these values were much lower than those of the field capacity of the landfilled material (36-39 wt.%). This means that raw WG had still an available retention capacity for storage of percolating water. The high capillary rise of compacted WG promotes water transport from the interior of the landfill and evaporation from the landfill surface.

No significant differences were found to occur in the chemical composition between the material sampled from the boreholes and the raw wastes (Table 1). There was no regularity (Fig.2), either in the vertical distribution of phosphates and fluorides (both easily soluble in water). It is very difficult to determine the changes in the macrostructure of the landfill, because infiltration and leaching occur predominantly in the microstructure of the WG. Low concentrations of phosphates and fluorides in groundwater (compared to that of sulfates) should be attributed to two major factors:

(1) small infiltration rate, and (2) chemical precipitation (in the forms of calcium phosphate and calcium fluoride) in the alkaline bottom layer (lime sludge and clinker wastes) of the higher part of the landfill.

A detailed study carried out on the deposited material enabled the total Y+LS resources in the landfill to be determined. They amount to 9200 tons. Among them are 220 tons of yttrium and 37 tons of europium [1]. If this amount were recovered, it would cover the 13-year Y+LS demand of the Polish industry. Recoverable gypsum resources are estimated to be as high as 1.45 million tons.

Taking those facts into account, a joint concept has been developed which enables recovery of Y+LS and manufacture of building gypsum from WG deposited on the landfill [2,3]. The flow chart and mass balance of the WG processing

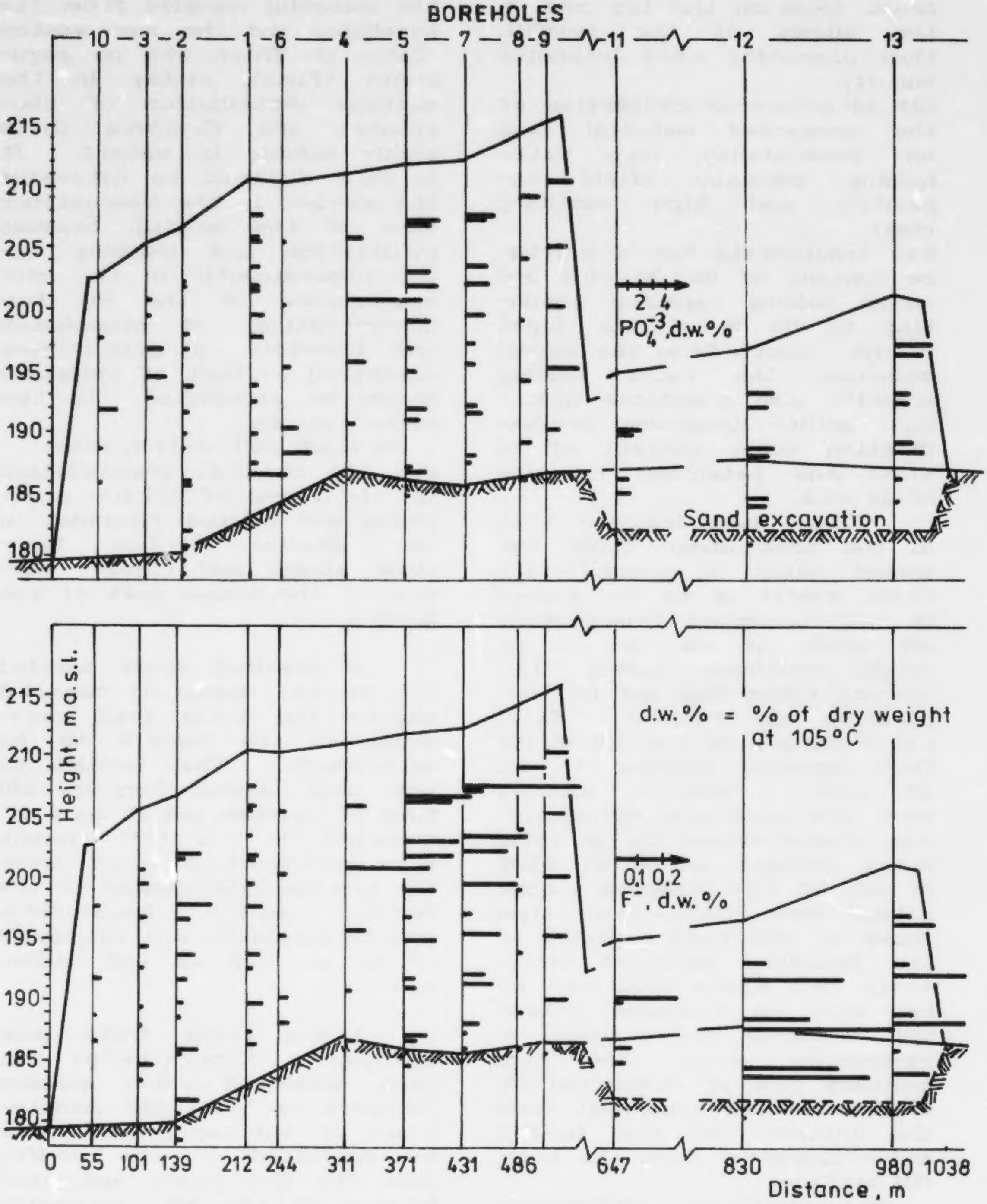
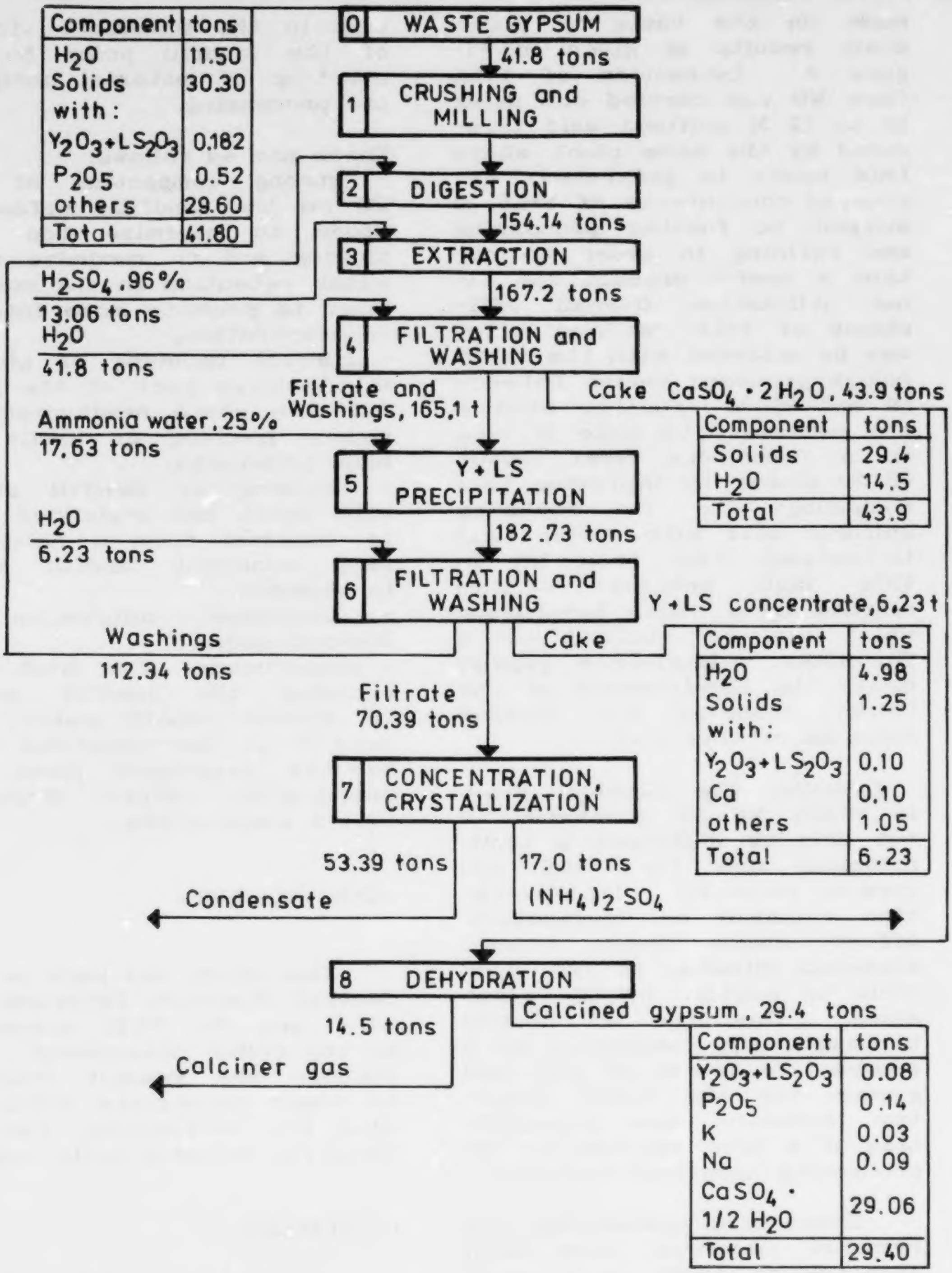


FIG. 2 DISTRIBUTION OF WATER-SOLUBLE FLUORIDES AND PHOSPHATES IN LANDFILL PROFILE


0 WASTE GYPSUM
41.8 tons
1 CRUSHING and MILLING
2 DIGESTION
154.14 tons
3 EXTRACTION
167.2 tons
4 FILTRATION and WASHING
H_2SO_4, 96%
13.06 tons
H_2O
41.8 tons
Filtrate and Washings, 165,1 t
Cake $CaSO_4 \cdot 2H_2O$, 43.9 tons
Ammonia water, 25%
17.63 tons
5 Y+LS PRECIPITATION
182.73 tons
H_2O
6.23 tons
6 FILTRATION and WASHING
Y+LS concentrate, 6.23 t
Washings
112.34 tons
Cake
Filtrate
70.39 tons
7 CONCENTRATION, CRYSTALLIZATION
53.39 tons
17.0 tons
Condensate
$(NH_4)_2SO_4$
8 DEHYDRATION
Calcined gypsum, 29.4 tons
14.5 tons
Calciner gas

Component	tons
H_2O	11.50
Solids with:	30.30
$Y_2O_3+LS_2O_3$	0.182
P_2O_5	0.52
others	29.60
Total	41.80

Component	tons
Solids	29.4
H_2O	14.5
Total	43.9

Component	tons
H_2O	4.98
Solids with:	1.25
$Y_2O_3+LS_2O_3$	0.10
Ca	0.10
others	1.05
Total	6.23

Component	tons
$Y_2O_3+LS_2O_3$	0.08
P_2O_5	0.14
K	0.03
Na	0.09
$CaSO_4 \cdot 1/2\,H_2O$	29.06
Total	29.40

FIG.3 FLOW CHART AND MASS BALANCE OF WASTE-GYPSUM PROCESSING

made on the basis of pilot-scale results is given in Figure 3. Extraction of Y+LS from WG was carried out using 10 to 12 % sulfuric acid (produced by the same plant where this waste is generated). Recovered concentrate of Y+LS is subject to further processing and refining in order to obtain a useful product for final utilization. Overall efficiency of Y+LS recovery which may be achieved with the technology proposed varies between 50 and 60 %. Further studies are necessary to make it rise to a reasonable level (about 80 %) either by improving this technology or by replacing sulfuric acid with nitric acid to extract Y+LS from WG. In this last process, calcium nitrate is a major by-product which can be utilized as a fertilizer. Recovered gypsum meets the requirements of the Polish Standard for binding material of this kind.

Actually, the chemical plant in which WG is generated is not able to implement a technological line for Y+LS and gypsum recovery. Implementation requires an investement effort which, under today's economic climate, is not possible to sustain by the plant alone. Thus the WG landfill is temporarily considered as a prospective source of Y+LS and gypsum for the Polish industry. Recently, new possibilities of a joint-venture for WG processing have been examined.

Short-term operational and remedial measures have been proposed in order to eliminate (or, at least, minimize) further environmental pollution in the immediate vicinity of the landfill prior to the start-up of material stripping and processing.

These are as follows:
- strong compacting of the WG on the landfill surface in order to minimize top dust blowing and to maximize rainwater retention in the surface layer to promote more intensive evaporation,
- current covering of sludges in the lower part of the landfill with waste hemihydrate to reduce leaching of easily soluble pollutants,
- covering of landfill slopes with earth and stabilized waste material from a neighbouring municipal landfill which is obsolent,
- biological cultivation of covered slopes,
- construction of a ditch surrounding the landfill slopes to collect runoff water, and send it to the industrial wastewater treatment plant for purification before discharge into a watercourse.

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OBSTACLES AND ISSUES IN SOURCE REDUCTION OF CHLORINATED SOLVENTS-SOLVENT CLEANING APPLICATIONS

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ABSTRACT

The Source Reduction Research Partnership (SRRP) is a unique joint venture of The Metropolitan Water District of Southern California and the Environmental Defense Fund. The partnership is sponsoring a study to estimate the potential for source reduction of chlorinated solvents, contaminants commonly found in ground and surface water system across the United States.

The project focuses on a particular chemical class, the chlorinated solvents, and targets principle solvent using industries including metal cleaning, dry cleaning and textile processing, electronics, paint stripping and coating, aerosols, chemical manufacturing and intermediates, and adhesives. The chlorinated solvents that are addressed in the course of study are: trichloroethylene (TCE), 1,1,1-trichloroethane (TCA), methylene chloride (METH), perchloroethylene (PERC), and trichlorotrifluorocarbon (CFC-113).

The project team has developed detailed industry profiles that will include a discussion of source reduction measures, which will reduce solvent use and toxic discharges in a multimedia fashion. Source reduction options that will be addressed in the course of the project include chemical and production substitution, process control and process changes, and housekeeping measures. Field interviews will also be conducted to verify information. Finally, the source reduction potential will be estimated taking into account institutional and economic considerations.

This paper will present a discussion of the obstacles that may be encountered in implementation of the source reduction options in solvent cleaning applications.

INTRODUCTION

Cleaning with chlorinated solvents is a common practice in many diverse sectors of industry. As much as 311 thousand metric tons (mt) of chlorinated solvents is used annually for this purpose (Yazdani, 1988). All five major chlorinated solvents--PERC, TCE, METH, TCA and CFC-113--are used in cleaning applications. Solvent cleaning is normally required before assembly, fabricating, painting or welding. It can also be used to reduce contamination in downstream production processes. It should be noted that the solvent cleaning process is a significant source of chlorinated solvent emission and hazardous waste generation.

Solvent cleaning can be classified into two major categories: cold cleaning and vapor degreasing.

Cold cleaning is used to remove drawing compounds, cutting and grinding fluids, polishing and buffing compounds and miscellaneous contaminants such as metal chips. Cold cleaning techniques include wiping, dipping, spraying, soaking, swabbing, immersing, brushing and ultrasonic agitation. Cold cleaners are the simplest type of cleaner. In some cases, blends of solvents such as chlorinated solvents and alcohols may be considered for cold cleaning applications. About one-third of chlorinated solvents is devoted to cold cleaning (Yazdani, 1988).

The vapor degreasing differs from cold cleaning in that it is normally conducted at the boiling temperature of the solvent. In general, a vapor degreaser is a steel tank with a stream or electrical heating coil below the liquid level and a water jacketed vapor cooling and condensing zone above the vapor level. The work piece is placed in the vapor zone. Boiling solvent vapors rise inside the tank to the level of the primary condensing coils. Solvent vapors condense on the cooler workload as it enters the vapor zone and dissolves and removes the contaminants. When the surface temperature of the object reaches that of the vapor, condensation ceases and cleaning is completed. Impurities accumulate in the sump.

PURPOSE

The chlorinated solvents, a class of interrelated chemicals is currently under regulatory scrutiny for a variety of reasons (Wolf et al, 1987).

Chlorinated solvent cleaning is a source of release of hazardous substances into the environment. There are two major loss mechanisms in solvent cleaning operations. The first--emissions to the atmosphere--are process emissions which are usually significant fractions of total emission up to 95 percent. The second loss mechanism is the waste generation which can constitute between 5 to 15 percent of solvent loss (SRRP, 1988). This implies that virtually all the solvent used is emitted to the atmosphere.

Solvent emissions can occur both directly or indirectly from all types of solvent cleaning equipment. Major causes of emissions include loss of solvent from the cleaning tank due to diffusion, carry out of solvent on cleaned parts, and leaks from tanks and associated equipment.

The hazardous waste generated in the cleaning processes include contaminated liquid solvent, bottoms from stills when on-site recycling is practiced, and bottom sludge that arises in cleaning degreaser tanks. Nowadays, generators commonly employ the services of an off-site recycler or do recycling on-site.

In the course of the study, a variety of source reduction options for chlorinated solvents has been examined in the solvent cleaning industry. These fall into the general categories of chemical substitution, process substitution, recovery and reuse of vapors, recycling of waste solvent, and operating practices. The two most attractive options, that is: chemical substitution and process substitution are presented in Table 1 and are discussed in more detail in the following sections. The result of the analysis suggest that such measures are complex and that attention need to be paid in order to avoid unexpected effects.

APPROACH

In what follows, a substitution analysis of chlorinated solvents in cleaning operations is presented. This is limited to the technical suitability dimension. Other dimensions, such as cost and health effects are beyond the scope of this analysis. These sections will discuss the available substitutes, will specify the contaminants that can be removed and the characteristics that the alternative solvents must possess to meet reasonable standards in cleaning.

Problems Encountered

As Table 1 summarizes, there are a variety of source reduction options to replace chlorinated solvents in the solvent cleaning industries. In some cases, the various options themselves may have adverse features which would not allow for complete replacement of the chlorinated solvents in all sectors.

Table 1. Source Reduction Options for Chlorinated Solvents in Cleaning Applications

Chemical Substitution	Process Substitution
° Low Molecular Weight Organic Solvents	° Aqueous Cleaning
° High Molecular Weight Organic Solvents	° Emulsion Cleaning
° Chlorofluorocarbons (CFCs) and Their Blends	

A. Chemical Substitution

In principle, an ideal substitution would consider all possible substitutes and compare them along three dimensions. The first dimension is technical suitability. All candidates should be compared in terms of their capability to accomplish a specific task. The second is economic. The complete cost analysis of a substitute includes the cost of raw material, associated equipment, process changes, regulatory requirements and disposal. The third dimension is health implications. The possible consequences of producing, using, and disposing of each candidate. Human health impacts based on toxicological data for each substance would also be necessary. In this paper, we focus on the first dimension, the technical suitability.

The effects of substitution are complex and can be unexpected since possible alternatives to a hazardous chemical may themselves be hazardous but in a different way, and there may be no valid way to compare them.

In cleaning applications, there are a number of chemicals that are technically feasible substitutes for both cold cleaning and vapor degreasing applications (SRRP, 1988; Yazdani, 1988).

Low molecular weight solvents such as aliphatic, aromatic and oxygenated solvents are possible chemical substitutes for chlorinated solvents. Most of these solvents show good solvency characteristics, however, they have several limitations such as low vapor pressure, flammability and are considered precursors to photochemical smog (Table 2).

They may be used to clean surfaces with typical contaminants susceptible to solvent removal including most greases, oils, waxes, resins, and polymers. These chemicals are presently used as simple substitutes for halogenated solvents in cold cleaning applications. No major equipment modification is required, the solvents

Table 2. Common Solvents Used For Cleaning

Type of Solvent	Solvent	Solvency for Removing Soils	Flash Point, F	Boiling Point, F (Range)	Solubility (wt. % of H_2O at ∞ 77°F	Wetting Index $\left(\frac{1000}{\mu\gamma}\rho\right)$
Alcohols	Ethanol (95 percent)	Poor	60	165 to 176	∞	30
	Isopropanol	Poor	55	179 to 181	∞	75
	Methanol	Poor	58	147 to 149		
Ketones	Acetone	Good	<0	132 to 134		
	Methyl ethyl ketone	Good	28	174 to 176		
Aliphatic Hydrocarbons	Heptane	Good	<20	201 to 207		
	Kerosene	Good	149	354 to 525		
	Stoddard	Good	105	313 to 380		
	Mineral Spirits 66	Good	107	318 to 382		
Aromatic Hydrocarbons	SC 150	Good	151	370 to 410		
	Toluene	Good	45	230 to 232		
	Turpentine	Good	91	314 to 327		
	Xylene	Good	81	281 to 284		
Chlorinated Solvents	METH	Excellent	None	104 to 105.5	.15	108
	PERC	Excellent	None	250 to 254	.01	57
	TCA	Excellent	None	165 to 194	.05	65
	TCE	Excellent	None	188 to 190	.02	87
	CFC-113	Good	None	117	.01	126
Water	-	Good	-	212	∞	14

Source: Marinello, 1980; Wolf et al, 1987.

Note: The solubility parameter gives an indication of the solvent power. The lower the value, the milder the solvent. The wetting index reflects the ability of the solvent to penetrate blind spaces in a part and float off the debris. The higher the index, the better the solvent accomplishes these ends. The boiling point of each solvent is important because the relative volatility of a solvent is given by the inverse order of the boiling point (i.e., the higher the boiling point, the less volatile the solvent).

show high solvency for common contaminants and chemical compatibility with all ferrous and nonferrous metals (SRRP, 1988).

Organic solvents have several limitations. They cannot be used in enclosed systems because of solvent vapor build up. These solvents can not be used in vapor degreasing applications because of their flammability. Another disadvantage of these solvents is that they have short atmospheric lifetimes and they form precursors that contribute to photochemical smog.

High molecular weight organic solvents such as terpenes, N-methyl pyrrolidene (NMP) and dibasic esters (DBE) are very new to the solvent cleaning market and are not widely used. These chemicals are considered biodegradable substances by their manufacturers and are rated combustible due to their flash point by the National Fire Protection Association. The flash point of Bioact DG-1 (a terpene product marketed by Petroferm, Inc.) is 47°C (117°F). These substances because of their combustible nature should be used at room temperature. Furthermore, a terpene supplier contends that the parts need to be washed with water afterwards to remove the terpene residue, which are too heavy to volatilize. This in itself may pose some problems since the stream may have to be handled properly (i.e. pretreated) prior to sewer discharge. To overcome the flammability problem, nitrogen inerting systems are proposed which will add to the expense of the unit. It should be noted that at this time, not much is known about the toxicity of these chemicals and it is not clear if they can be recycled for reuse.

The new CFC that is under investigation as a replacement for CFC-113 and other chlorinated solvents is CFC-123, which has shown good solvent power, stability, low surface tension, and low ozone depletion potential, because it contains hydrogen. CFC-123 has a low boiling point (27.7°C) which is advantageous for some applications such as cold cleaning but disadvantageous for others. A consortium of CFC producers has organized a toxicity testing program to test the chemical for chronic toxicity effects. New CFCs would not be commercially available for the next five years. Presently there is no production process for production of CFC-123 and there is active research to identify a process which gives reasonable yield (CMR, 1988).

Some other solvent blends such as Freon SMT and ISC-108 are available as partial substitutes for chlorinated solvents since they contain a small percentage of chlorinated solvents. The Freon SMT which has been marketed by DuPont has 68 percent CFC-113, 25 percent 1,2 Dichloroethylene and 6 percent alcohol. ISC-108 which has 0.4 percent TCA by weight in an alkaline solution with a surfactant, is considered a biodegradable compound and requires neutralization prior to discharge to the sewer.

B. Process Substitution

A number of processes are available and are potential for chlorinated solvent degreasing. Aqueous cleaning is popular for removing contaminants from various media.

The water based cleaning methods usually employ simple hot water with some additives in combination with mechanical, electrical or ultrasonic energy. Aqueous cold cleaning is popular for removing contaminants from metal furniture, fabricated product, and transportation equipment.

Water, although it may be used in a variety of different industries, can not be substituted for cleaning of products where its use may induce material or substrate corrosion. At the same time, because of high surface tension of water (Table 2), parts with small interstices may not be effectively cleaned. Aqueous cleaning can remove potentially damaging chloride residues in industrial soils that can not be removed by vapor degreasing (SRRP, 1988). The extent to which aqueous cleaning can replace solvent applications is not known; complete substitution is probably not possible and applicability needs to be determined on a case by case basis.

Water has several disadvantages. It has a low solubility for organic soils such as greases. It evaporates slowly, it conducts electricity, it has high surface tension and it causes rusting of ferrous metals and staining of nonferrous metals. Aqueous cleaning is likely to leave residual water on cleaned parts which can promote corrosion. Manufacturers of aqueous systems sometimes recommend the use of a final rinse with rinse inhibitor to resolve this problem. Drying of parts can be achieved using a hot air knife, soak tank or rotary drum washers (SRRP, 1988).

Also, water which is a nonhazardous material becomes hazardous when used and requires appropriate handling such as pretreatment prior to discharge to the sewer. In spite of the pretreatment costs, present equipments need to also be modified for use of the aqueous cleaning process.

Emulsion cleaning is another possible substitute for chlorinated solvent cleaning applications. Emulsion cleaning is primarily used in the process of cleaning metal parts to remove pigments or impediment drawing compounds, lubricants, cutting fluids and metal chips. Emulsion is not a substitute for vapor degreasing since it leaves a light film residue or oil onto the parts. This film may be good for rust protection or bad for maintenance and repair operations that require parts without oil or residue. Sometimes subsequent cleaning with alkaline cleaners is necessary.

RESULTS

The chlorinated solvents used today for cleaning purposes amounts to 311 thousand mt. Some source reduction opportunities have been examined in this article.

Chemical substitution on the average has "medium" (5-10 years) potential. Alternative chemical substitutes probably cannot replace chlorinated solvents in all applications, and such substitutes may have drawbacks making one hundred percent replacement of chlorinated solvents unlikely. In many cases, testing of alternatives, some of which are new to the market may extend the time frame for substitution. In most cases, R&D may be required to thoroughly investigate conversion potential. We believe such testing will result in a medium time frame for implementation.

Process substitution, especially conversion to aqueous and emulsion cleaning techniques--is possible where such conversions are technically satisfactory. Mechanical cleaning methods and cold cleaning with other solvents are other examples of process substitutions that can have limited applications. Overall, we believe process substitution has "medium" potential. Because equipment conversion is required to accomplish process substitution, a 5 to 10 year implementation will be necessary.

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Use of EPA's Synthetic Soil Matrix (SSM) in the Evaluation and Development of Innovative Soil Treatment Technologies

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ABSTRACT

This paper reviews the development and use of EPA's synthetic soil matrix or SSM. This surrogate soil was developed to be broadly representative of contaminated soils occurring at CERCLA sites. It is composed of natural soil fractions such as clays, topsoil, sand, gravel, and silt, and is spiked with a variety of organic and inorganic chemicals known to occur frequently at CERCLA sites. SSM has been used to test and compare the treatment efficiencies of various types of soil treatment technologies, including emerging and innovative systems. Currently, it is being spiked with gasoline, diesel, and waste oil and used to evaluate the application of soil washing to the remediation of contaminated soils and fill material at petroleum underground tank sites where spills or leaks have occurred.

BACKGROUND

The USEPA's Risk Reduction Engineering Laboratory is currently evaluating several innovative treatment technologies for contaminated soil from Superfund and RCRA sites. Soil washing, dechlorination, stabilization, vitrification, thermal desorption, incineration, biodegradation, vacuum extraction, and steam stripping are examples of technologies that have been recently evaluated.

In 1987, a program was initiated to develop and produce a standard soil for treatability testing. The goal was to develop a consistent and standard test material that could be used to test and compare the treatment efficiency of several different types of technologies, including emerging and innovative treatment systems. After considering several alternatives, EPA decided to develop a synthetic soil matrix (SSM) that could be easily reproduced from readily available stocks of clay, sand, gravel, and other soil materials. This would provide a long term source of the soil for EPA's research purposes as well as allow other scientists the opportunity to obtain it or reproduce it for their own research programs.

SSM DEVELOPMENT

Development of the SSM began in the spring of 1987 with a review of the soil types that typically are encountered at Superfund sites. Information on soil type was gleaned from EPA Records of Decision, as well as from a study of eastern US soil composition. From this review it was determined that the soil should have a well-stratified grain size distribution containing at least 25% fine clay-sized particles, a moderate cation exchange content of 30-50 meq/100 g, a total organic carbon content of 3-6%, a pH of 5-8, and a 10-20% moisture content. Following several weeks of bench scale formulation tests which sought to optimize the soil for these parameters, a final formula for the basic (unspiked) SSM emerged, as shown in Table 1.

Thirty thousand pounds of the soil were prepared from these dry ingredients in the early summer of 1987 at a sand and gravel quarry in southwestern Ohio using standard quarry materials handling equipment. The soil (which had a 5% moisture content) was packaged in 55-gallon steel drums, 500 pounds to the drum, and transported to EPA's Center Hill Research Facility in Cincinnati. There it was spiked with additional moisture and seventeen selected organic and inorganic chemicals known to frequently occur in contaminated soils at Superfund sites. The chemicals were added to the SSM at different levels to produce a series of four spiked formulations that have become known as SSM-I, SSM-II, SSM-III, and SSM-IV. The formula for each of these SSMs is given in Table 2.

Each of the SSMs so prepared was used in the summer of 1987 to test and compare the treatment efficiency of five technologies, namely soil washing, dechlorination, stabilization, thermal desorption, and incineration. These technologies were selected because they were believed to have the greatest potential for application to soils that would be banned from landfilling as a result of the Hazardous and Solid Waste Act Amendments (HSWA).Results of these tests have been recently published. [1-6]

EDISON PRODUCTION FACILITY

In the fall of 1988, EPA moved the SSM production facility from its original location in Cincinnati to EPA's research facility in Edison NJ. [7] New mixing equipment was purchased and the system was re-engineered to optimize the soil/contaminant blending process and reduce potential workplace hazards. This facility was completed in October of 1988 and is currently operational. A new 30,000 pound supply of unspiked SSM is stockpiled at the NJ facility for use in future SSM-related studies. The new facility in Edison consists of three functional areas or zones:

1. The mixing area (exclusion zone): This is the area where chenicals are blended with the soil. It includes a 10 cubic foot capacity Marian tilt-tub mixer with explosion proof motor, access platform, ventilation system, bermed floor, work benches, weighing and measuring equipment, umbilical air-line support for four operators in level B, and other facilities and equipment ancillary to the batch production of SSMs.

2. The decontamination area (contamination reduction zone): This area acts as a buffer between the exclusion and clean zones to prevent the clean area from getting contaminated.

3. The clean/support area (clean zone): This area is designated for all support services. It includes an office trailer, storage cabinets for supplies, a storage area for the clean SSM supply, emergency equipment, and phones.

EPA has prepared a video, brochure, and user's manual covering the operations and availabililty of SSM from this facility. [8-10] These resource materials are available from the Risk Reduction Engineering Laboratory in Edison (contact Richard Traver at 201/321-6677).

MODIFIED SSM FOR THE SITE PROGRAM

In late 1988, a modified version of SSM formula IV containing only chrome, zinc, tetrachloroethylene, bis(2-ethylhexyl)phthalate, and anthracene at relatively high dosage levels was prepared and used to pretest the efficiency of an innovative centrifugal plasma torch thermal treatment system for contaminated soils. This technology, under development by Retech of California, provides both destruction of organics and vitrification of residual metals within the molten soil mass.

For this test, the SSM was required to have a minimum analyzable content for each of the five selected analytes, in order to insure the potential demonstration of RCRA's 99.99% destruction and removal efficiency (DRE) performance standard for high temprature thermal treatment devices. The formula for the SSM used in this program is given in Table 3. The table shows the specified minimum composition of this batch, the expected concentrations (based on dosages applied), and the average actual concentrations achieved as defined by chemical analysis of 16 samples taken from the batch. Although the tetrachloroethylene content of the batch was considerablly higher than expected, the rest of the analytes were close to the expected concentrations and the batch was accepted. The high contaminant levels in the SSM provided wide windows of opportunity for evaluating the system's ability to deliver 4-nines DRE on the organics and adequate metals retention or capture in either the vitrified soil residue or the air pollution control system.

Testing of the Retech unit with the SSM was carried out under the SITE program in the spring of 1989. Results of this test program have not yet been made available, but are expected to be released later this year.

UST SOIL TREATMENT R&D

EPA's Risk Reduction Engineering Laboratory has been actively involved at its Releases Control Branch in Edison, New Jersey with research and development efforts to address the problem of leaking underground storage tanks (USTs). Under this effort, EPA is currently evaluating several corrective action technologies for cleaning up soil contaminated by the release of petroleum products from USTs. Several key concerns for applying these technologies to petroleum contaminated soils are the effectiveness of the technology to remove the contaminants from the soil, the management of the residuals, and the total system costs.

As part of the research program, soil washing technology is being evaluated to determine the feasibility of applying this technology to the cleanup of soils contaminated with petroleum products. this process has been shown to be effective for the removal of organics and inorganics common to petroleum products, namely xylene, ethylbenzene, toluene, benzene, and lead.

At the present time, about 6000 pounds of the clean SSM are being used to prepare a series of new SSM test soils spiked with petroleum products for use in the soil washing feasibility study. The SSM will be spiked with various amounts of gasoline, diesel, and waste oil and used as the test matrix for bench and pilot scale demonstration tests. EPA's pilot-scale mini-soil washer will be utilized in the study. This unit is capable of processing 600 pounds of soil per hour; it was designed and constructed in 1988 from state-of-the-art specifications developed by RREL. The test program will be carried out at the Edison NJ facility, and in the field at UST sites of opportunity.

Results of this testing program should be available in late 1989.

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TABLE 1. BASIC SSM COMPOSITION

Soil Component	Weight %
Clays	
montmorillinite	5
kaolinite	10
Sand	31
Gravel (No.9)	6
Silt	28
Topsoil	20

TABLE 2. TARGET CONTAMINANT CONCENTRATIONS FOR SSM, MG/KG

Analyte	SSM-I (High organic, low metal)	SSM-II (Low organic, low metal)	SSM-III (Low organic, high metal)	SSM-IV (High organic, high metal)
Volatiles				
Acetone	6,800	680	680	6,800
Chlorobenzene	400	40	40	400
1,2-Dichloroethane	600	60	60	600
Ethylbenzene	3,200	320	320	3,200
Styrene	1,000	100	100	1,000
Tetrachloroethylene	600	60	60	600
Xylene	8,200	820	820	8,200
Semivolatiles				
Anthrecene	6,500	650	650	6,500
Bis(2-ethylhexyl) phthalate	2,500	250	250	2,500
Pentachlorophenol	1,000	100	100	1,000
Inorganics				
Arsenic (as As2O3)	10	10	500	500
Cadmium (as 3CdSO4 . 8H2O)	20	20	1,000	1,000
Chromium (as Cr(NO3)3 . 9H2O)	30	30	1,500	1,500
Copper (as CuSO4 . 5H2O)	190	190	9,500	9,500
Lead (as PbSO4 . PbO)	280	280	14,000	14,000
Nickel (as Ni(NO3)2 . 6H2O)	20	20	1,000	1,000
Zinc (as ZnO)	450	450	22,500	22,500

TABLE 3. SPECIFICATIONS FOR MODIFIED SSM-IV FOR THE RETECH DEMONSTRATION

Analyte	Specified minimum ppm	Expected ppm*	Actual ppm**
Tetrachloroethylene	1000	2075	3277
Anthracene	6500	7420	7361
Bis (2-ethylhexyl) phthalate	2500	3785	3702
Zinc	22500	26475	28306
Chromium	1500	1775	1898

* Based on dosage applied to soil

** Average of 16 samples analyzed

Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

PILOT-SCALE INCINERATION TESTING OF AN OXYGEN-ENHANCED COMBUSTION SYSTEM

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ABSTRACT

A series of demonstration tests of the American Combustion, Inc., Thermal Destruction System was performed under the Superfund innovative technology evaluation (SITE) program. This oxygen-enhanced combustion system was retrofit to the pilot-scale rotary kiln incinerator at EPA's Combustion Research Facility. This system's performance was tested firing contaminated soil from the Stringfellow Superfund Site, both alone and mixed with a hazardous coal tar waste (decanter tank tar sludge from coking operations — K087). Comparative performance with conventional incinerator operation was tested.

Test results show that compliance with the hazardous waste incinerator performance standards of 99.99 percent principal organic hazardous constituent (POHC) destruction and removal efficiency (DRE) and particulate emissions of less than 180 mg/dscm at 7 percent O_2 was achieved for all tests. The Pyretron oxygen-enhanced combustion system allowed in-compliance operation at double the mixed waste feedrate possible with conventional incineration, and with a 60 percent increase in charge weight than possible with conventional incineration.

INTRODUCTION

Under EPA's Superfund innovative technologies evaluation (SITE) program, several innovative waste treatment technologies are being evaluated to determine their applicability to Superfund site waste cleanup efforts. Under this program, EPA supports the evaluation while process vendors are responsible for the treatment process construction and operation.

A demonstration of the American Combustion, Inc., (ACI) oxygen-enhanced burner system (referred to as the Pyretron Thermal Destruction System) interfaced with the Combustion Research Facility's (CRF) rotary kiln incinerator system (RKS) was performed under the SITE program. This program was conducted using waste material excavated from the Stringfellow Superfund site near Riverside, California. In most tests the Stringfellow soil was combined with a high heating value listed hazardous waste, K087 (decanter tank tar sludge from coking operations).

PURPOSE

The objective of the demonstration tests was to provide data to evaluate three ACI claims regarding the Pyretron system:

- The Pyretron system with dynamic oxygen enhancement reduces the magnitude of the transient high levels of organic emissions, CO, and soot ("puffs") that occur with repeated batch charging of waste fed to a rotary kiln
- The Pyretron system is capable of achieving the RCRA mandated 99.99 percent destruction and removal efficiency (DRE) of principal organic hazardous constituents (POHCs) in wastes incinerated at a higher waste feedrate than conventional, air-only, incineration
- The Pyretron system is more economical than conventional incineration

This paper addresses only the first two objectives

APPROACH

As noted above, the demonstration tests were performed using a prototype Pyretron system retrofitted to the rotary kiln incineration system (RKS) at the CRF. A simplified schematic of this system is given in Figure 1.

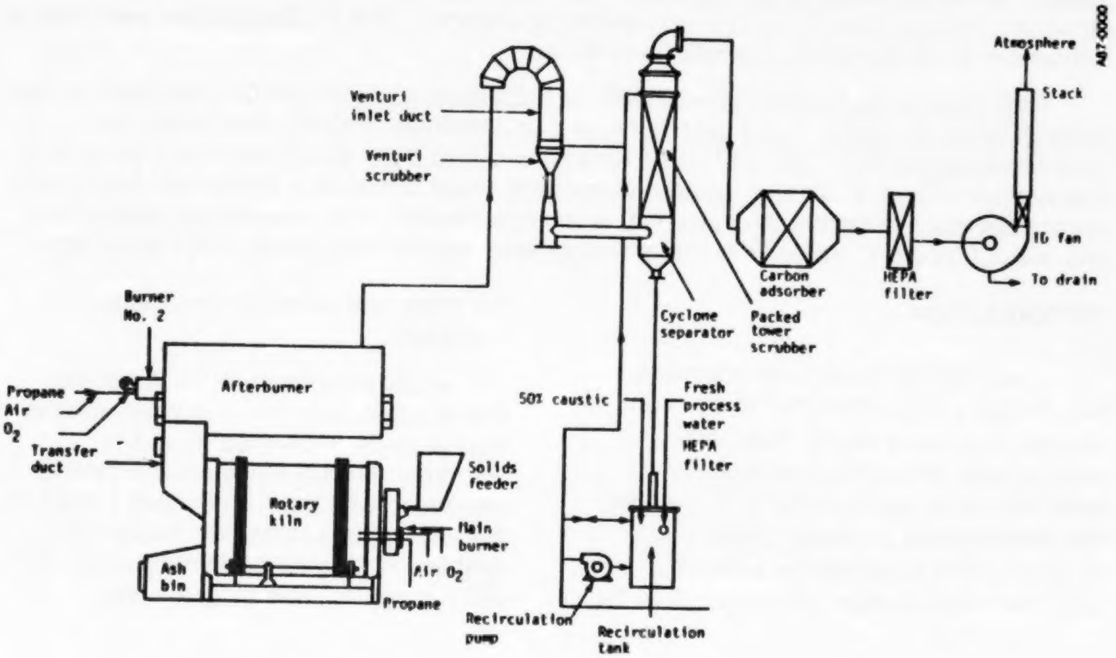
A87-0000
Atmosphere
Stack
Venturi inlet duct
Venturi scrubber
IG fan
To drain
Carbon adsorber
HEPA filter
Burner No. 2
Cyclone separator
Packed tower scrubber
Propane
Air
O_2
Afterburner
50% caustic
Fresh process water
HEPA filter
Transfer duct
Solids feeder
Rotary kiln
Main burner
Air O_2
Ash bin
Propane
Recirculation pump
Recirculation tank

Figure 1. CRF rotary kiln system.

The prototype Pyretron system retrofitted to the CRF RKS consisted of the following: a propane-fired burner installed at the waste feed end of the RKS kiln; a similar burner in the RKS afterburner; gas metering and control assembly (valve trains) for controlling propane, air, and oxygen flows to both burners; an oxygen supply consisting of a trailer-mounted liquid oxygen tank with evaporator; and a system for injecting water into the kiln to afford additional kiln temperature control.

The waste incinerated in these tests consisted of contaminated soil from the Stringfellow Superfund site mixed with the listed hazardous waste K087. The mixed waste contained 60 percent K087 waste and 40 percent Stringfellow soil. The K087 waste was included in the test mixture to give it heat content and thereby present a challenge to the incineration process. In addition, the K087 contributed to the POHCs in the waste mixture. The K087 waste contained several polynuclear aromatic hydrocarbon compounds in percent quantities. Six of these, naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, and fluoranthene were selected as the POHCs for the test program.

For these tests a fiber pack drum ram feeder system was used to feed waste to the kiln. This system feeds 5.7-L (1.5-gal) fiber pack drums in a cyclical batch charge operation. Drums contained between 4.1 and 7.9 kg (9 to 17 lb) of waste depending on the specific test underway.

Six tests were performed to supply data to evaluate the ACI claims. Since the ACI claims state that the Pyretron system offers superior performance when compared to conventional incineration, one set of operating conditions reflecting the limit of the capabilities of conventional incineration in terms of waste batch charge mass and total waste mass feedrate was tested.

The capability limits for conventional incineration were defined via several scoping tests. These tests confirmed that a waste feed schedule of 10.9 kg (24 lb) every 10 min resulted in unacceptable transients in kiln exit flue gas CO levels. These transient CO puffs survived passage through the afterburner and gave unacceptable CO spikes at the stack. A waste feed schedule of 9.5 kg (21 lb) every 12 min resulted in acceptable incinerator operation. This feed schedule was defined to be the capability limit of conventional incineration and was denoted the optimum conventional operating condition. Two emissions tests (replicates) were performed at this condition.

The other four tests were performed with the Pyretron system in operation. The optimum conventional operating condition was repeated with the Pyretron system. Then a waste feed schedule of 15.5 kg (34 lb) every 19.5 min was tested with the Pyretron system to evaluate the ACI claim that the Pyretron system can reduce the magnitude of transient puffs. Finally, a waste feed schedule of 9.5 kg (21 lb) every 6 min was tested with the Pyretron system to evaluate the ACI claim that higher waste feedrates would be possible with the Pyretron system. Two tests (replicates) were performed at this last test condition as well.

Table 1 summarizes the incinerator operating conditions tested.

RESULTS

Figure 2 plots the variation in incinerator operating parameters for the conventional incineration attempt to feed

TABLE 1. AVERAGE INCINERATOR OPERATING CONDITIONS FOR THE TESTS PERFORMED

	Waste			Kiln exit		Afterburner exit	
Operation	Charge weight, kg (lb)	Charge interval, minutes	Feedrate, kg/hr (lb/hr)	Temperature °C (°F)	Flue gas O_2 %	Temperature °C (°F)	Flue gas O_2 %
Conventional, scoping	10.9 (24)	10	65.5 (144)	1,027 (1,880)	9.9	1,121 (2,050)	6.4
Conventional, optimum	9.5 (21)	12	47.7 (105)	954 (1,750)	13.3	1,121 (2,050)	7.7
Conventional, optimum replicate	9.5 (21)	12	47.7 (105)	921 (1,090)	12.8	1,121 (2,050)	7.4
Pyretron, at conventional optimum	9.5 (21)	12	47.7 (105)	1,035 (1,895)	17.6	1,121 (2,050)	15.2
Pyretron, increase charge mass	15.5 (34)	19.5	47.7 (105)	963 (1,765)	14.5	1,121 (2,050)	15.0
Pyretron, optimum	9.5 (21)	6	95.5 (210)	979 (1,795)	13.9	1,121 (2,050)	14.0
Pyretron, optimum replicate	9.5 (21)	6	95.5 (210)	979 (1,795)	14.6	1,121 (2,050)	15.3

[a] Replicate tests.

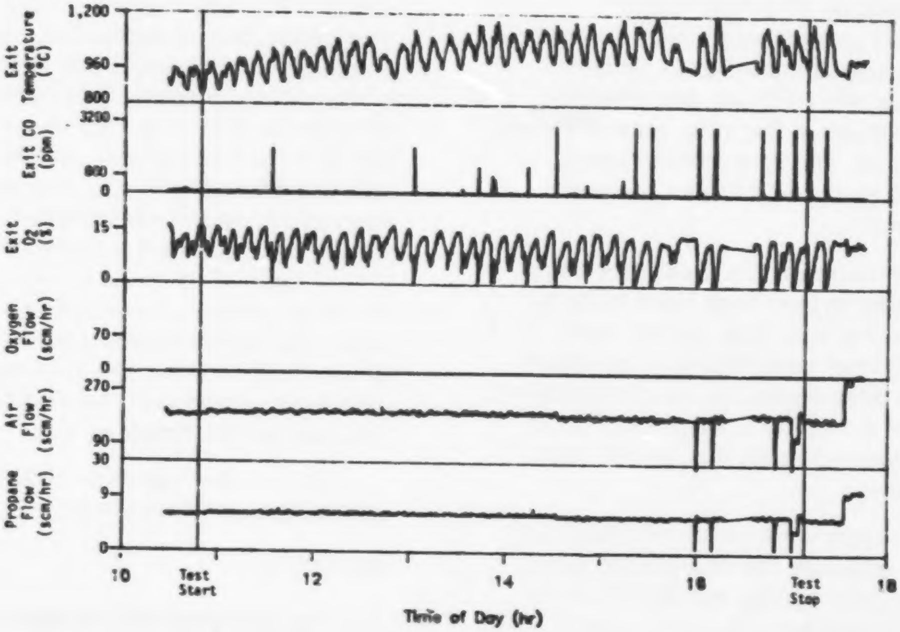

Figure 2. Kiln data for the conventional incineration scoping tests: 65.6 kg/hr (10.9 kg every 10 min).

10.9 kg (24 lb) of mixed waste every 10 min. The figure shows that, early in the test period, kiln exit temperature varied from about 870 to 980°C (1,600 to 1,800°F) over a charge cycle. Kiln exit O_2 ranged from about 7 to 16 percent O_2 over a cycle, and kiln exit CO levels were generally low. However, intermittent CO spikes up to 2,200 ppm occurred. As this test proceeded, kiln temperature increased such that, after about 3 hours of operation, kiln exit temperature was ranging from 980 to over 1,150°C (1,800 to over 2,100°F) over a charge cycle. Kiln exit flue gas O_2 peaked at about 15 percent just prior to initiating a batch charge, but decreased to 0 as the puff of volatilized waste from a charge filled the kiln. Kiln exit CO levels peaked at about 3,000 ppm under these depleted O_2 conditions. These CO puffs survived through the afterburner and resulted in CO peaks of above 100 ppm at the stack.

In contrast, operating conditions for conventional operation were much more controlled with a waste feed schedule of 9.5 kg (21 lb) every 12 min, as shown in Figure 3. At stabilized operation, kiln exit temperature ranged from about 900 to 1,080°C (1,650 to 1,970°F) over a charge cycle. Kiln exit CO peaks were less than about 50 ppm with the one exception, a spike early in the test. These were reduced to less than 10 ppm at the stack after passage through the afterburner.

Figure 4 shows the variation in operating parameters for the Pyretron system test at an increased charge mass of 15.5 kg fed every 19 min. For this test, average kiln exit temperature was comparable to the conventional incineration optimum condition test at about 960°C (1,765°F), though

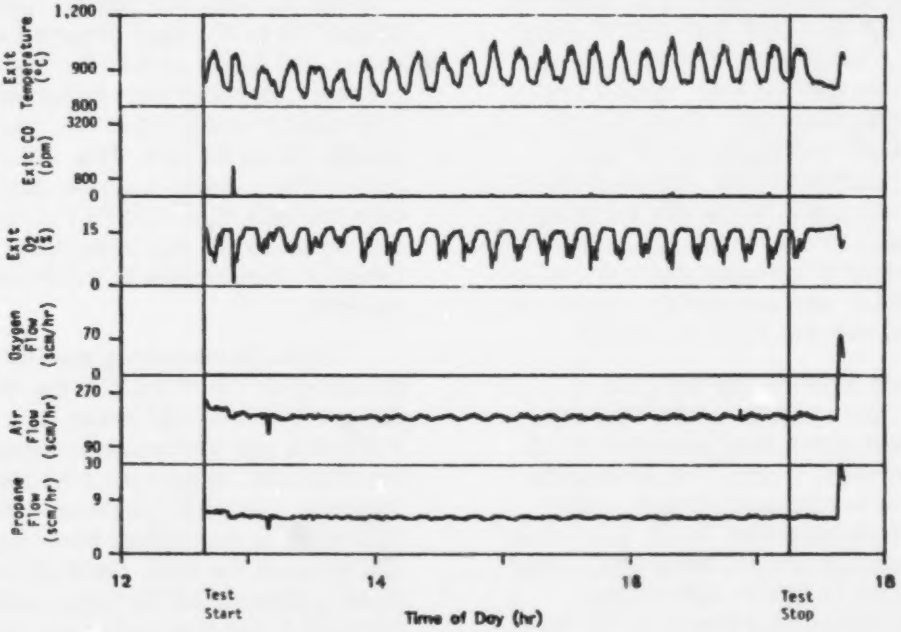

Figure 3. Kiln data for the optimum conventional incineration tests: 47.7 kg/hr (9.5 kg every 12 min).

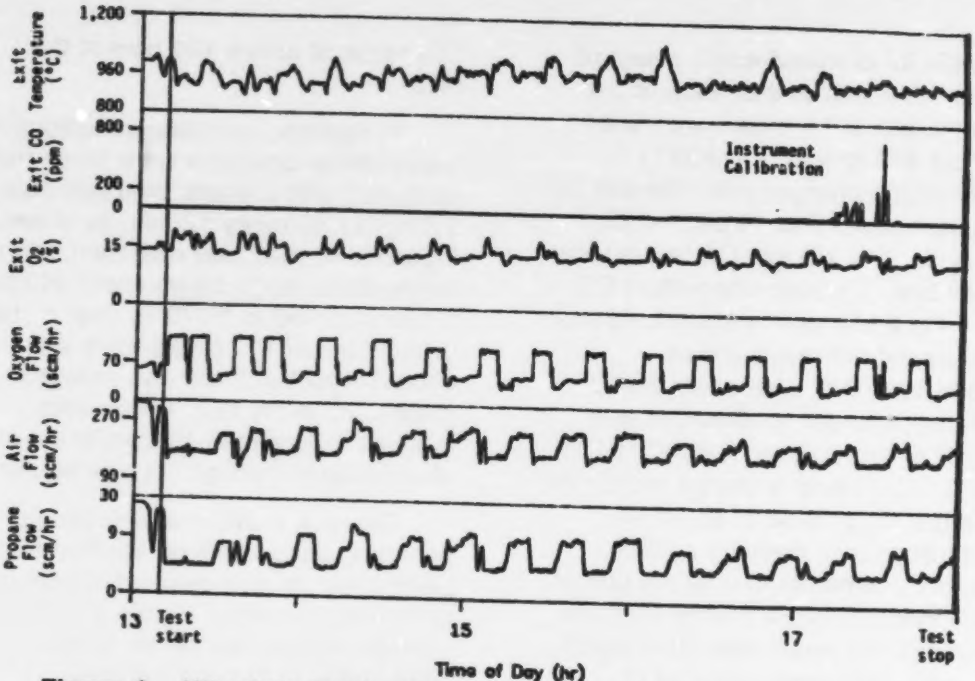

Figure 4. Kiln data for the Pyretron system test at increased charge mass: 47.7 kg/hr (15.5 kg every 19.5 min).

temperatures as low as 870°C (1,600°F) and as high as 1,065°C (1,950°F) were routinely experienced. Kiln exit flue gas O_2 generally ranged from about 13 to about 19 percent over a charge cycle. However, kiln exit flue gas CO was generally below 10 ppm. This test clearly established that a 60 percent increase in waste batch charge mass (9.5 to 15.5 kg) over the limit of conventional incineration was possible with acceptable emissions transients with the Pyretron system.

Figure 5 shows the variation in operating parameters for the Pyretron system test with a feed schedule of 9.5 kg (21 lb) every 6 min. This represents double the feedrate achievable under conventional operation. As shown in the figure, average kiln exit temperature was about 980°C (1,795°F) with routine variations from about 925°C (1,700°F) to about 1,035°C (1,900°F). Kiln exit flue gas O_2 generally ranged from 11 to 17 percent. Kiln exit flue gas CO peaks of about 100 to 300 ppm occurred when kiln exit O_2 fell below about 10 percent. However, for other than these periods, CO levels in the kiln exit flue gas were usually about 30 ppm. This test clearly shows that a waste feedrate double that possible with conventional incineration can be achieved with acceptable emission transients with the Pyretron system.

Table 2 summarizes the DREs achieved for the POHCs in the mixed Stringfellow soil/K087 waste at a location in the flue gas that would correspond to the stack discharge from a typical industrial rotary kiln incinerator. This location is at the packed tower scrubber discharge at the CRF. None of the POHCs designated for these tests were detected in the flue gas at this location. The DREs noted in Table 2 reflect method detection limits.

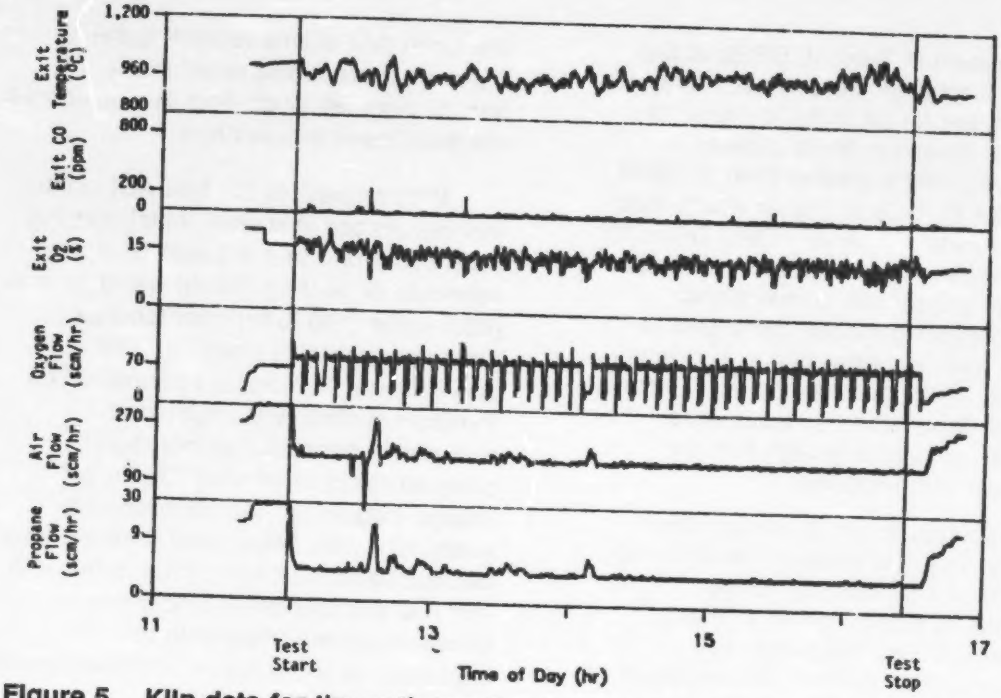

Figure 5. **Kiln data for the optimum Pyretron system tests: 95 kg/hr (9.5 kg every 6 min).**

TABLE 2. SCRUBBER DISCHARGE POHC DREs

	POHC DRE (%)					
	Naphthalene	**Acenaphthylene**	**Fluorene**	**Phenanthrene**	**Anthracene**	**Fluoranthene**
Test 3a (12-9-87)						
Train 1	>99.99934	>99.9975	>99.9945	>99.9985	>99.9951	>99.9979
Train 2	>99.99936	>99.9976	>99.9947	>99.9986	>99.9953	>99.9980
Test 3 (12-11-87)						
Train 1	>99.99924	>99.9967	>99.9933	>99.9984	>99.9945	>99.9974
Train 2	>99.9964	>99.984	>99.968	>99.9920	>99.974	>99.988
Test 4 (12–17–87)	>99.99896	>99.9955	>99.9937	>99.9979	>99.9933	>99.9960
Test 5 (1–14–88)	>99.99978	>99.99910	>99.9981	>99.99948	>99.9983	>99.9989
Test 6 (1-20-88)						
Train 1	>99.99989	>99.99958	>99.99914	>99.99976	>99.99922	>99.99949
Train 2	>99.99990	>99.99961	>99.99919	>99.99977	>99.99927	>99.99952
Test 6a (1-21-88)						
Train 1	>99.99991	>99.99965	>99.99930	>99.99980	>99.99935	>99.99953
Train 2	>99.99990	>99.99961	>99.99923	>99.99978	>99.99929	>99.99948

As shown in Table 2, DREs at the scrubber discharge were greater than 99.99 percent for all POHCs. In many instances, detection limits allowed establishing DREs greater than 99.9999 percent for POHCs at higher waste feed concentrations. Since all POHC DREs for all tests were >99.99 percent, no relative statement concerning conventional incineration performance compared to Pyretron system performance is possible. The good DRE performance in all tests is understandable since all tests were performed at relatively high kiln and afterburner temperatures.

Particulate levels in the scrubber discharge flue gas were in the 20 to 40 mg/dscm at 7 percent O_2 range regardless of test conditions. These levels were below the incinerator performance standard of 180 mg/dscm at 7 percent O_2.

The composite scrubber blowdown liquor and kiln ash samples from each test were analyzed for the test POHCs and other Method 8270 semivolatile organic hazardous constituents and none were detected. Since semivolatile organics were not detected in any residual sample, firing mode (conventional versus three conditions of Pyretron operation) had no measurable effect on residue composition.

CONCLUSIONS

The objective of the demonstration tests was to provide the data to evaluate the three ACI claims regarding the Pyretron system discussed in the Introduction, although only two objectives are addressed in this paper.

With respect to the first ACI claim, test results are inclusive. Initial scoping tests confirmed that a waste feed schedule of 10.9 kg (24 lb) every 10 min (65.5 kg/hr (140 lb/hr) total feedrate) gave unacceptable operation under conventional incinerator operation. The Pyretron system was capable of acceptable operation at increased charged mass of 15.5 kg (34 lb) but charge frequency was decreased to every 19.5 min. Thus, total feedrate was decreased to 47.7 kg/hr (105 lb/hr). Kiln exit flue gas CO levels under this condition were comparable to conventional incineration operation at the same overall waste feedrate.

With respect to the second ACI claim, test results clearly indicate that 99.99 percent POHC DRE was achieved with the Pyretron system with waste feedrate doubled over the limit established under conventional operation. Acceptable operation with the Pyretron system was achieved at a feed schedule of 9.6 kg (21 lb) every 6 min, or 95.5 kg/hr (210 lb/hr). Greater than 99.99 percent DRE for all POHCs, and particulate emissions of significantly less than 180 mg/dscm at 7 percent O_2 were measured.

Disclaimer

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THE PARTITIONING OF METALS IN ROTARY KILN INCINERATION

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ABSTRACT

This research project investigated the fate of trace metals in rotary kiln incineration with venturi- and packed tower-scrubber particulate- and acid gas-control. A test plan was developed, using a factorial experimental design, to study the partitioning of metals among kiln ash, scrubber water, flue gas particulate, and flue gas vapor. Synthetic waste formulations included the hazardous trace elements arsenic, lead, cadmium, chromium, and barium, as well as the non-hazardous trace elements copper, magnesium, bismuth and strontium, spiked into a clay absorbent material. The independent variables chosen for evaluation were chlorine content of the feed, kiln temperature, and afterburner temperature.

Cadmium, lead and bismuth appeared volatile over the range of kiln temperatures tested, while the other six metals displayed refractory properties. Of the three independent variables tested, feed chlorine content had the strongest effect on changes in metal partitioning across the tests; as chlorine content increased, metal volatilization appeared to increase, while scrubber efficiency for metals decreased.

INTRODUCTION

Metals, such as arsenic, barium, beryllium, cadmium, chromium, lead, mercury, nickel, and zinc are of concern in waste incineration because of their presence in many hazardous wastes and because of possible adverse health effects from human exposure to emissions. Incineration will change the form of metal fractions in waste streams, but it will not destroy the metals. As a result, metals are expected to emerge from the combustion zone essentially in the same total quantity as the input. The principal environmental concern centers around where and in what physical or chemical form the metals end up in the combustion system, i.e., bottom ash, air pollution control device (APCD) residues, or stack emissions.

Most interest has traditionally focused on stack emissions of metals. However, increasing attention is being given to the quality of residuals from incineration of metal-bearing wastes since disposal of these materials may be subject to restrictions on land disposal under the Hazardous and Solid Waste Act of 1984 (HSWA). (1)

A major role of the U.S. EPA Combustion Research Facility (CRF) in Jefferson, Arkansas is to perform research in support of regulatory development by the U.S. EPA Office of Solid Waste (OSW). Accordingly, the CRF has conducted research to study the partitioning of trace metals during the incineration of a metal-bearing surrogate waste. (2)

The testing described herein took place in the Rotary Kiln System (RKS) of the CRF, utilizing venturi- and packed tower-scrubbing for particulate- and acid gas-control. This research is part of a larger test program designed to evaluate the fate of metals in incineration using a variety of APCDs.

PURPOSE

Field studies to date indicate that emissions of metals from incinerators burning wastes of relatively low metal content probably do not pose an unacceptable level of risk. However, as the level of metals in wastes which are incinerated rises, there is concern that some incinerators could create unacceptable risk. Current regulatory thinking suggests implementation of metal emission limits and metal feed-rate limits, calculated using health risk levels and dispersion modeling.

Information gathered from the subject research will be used to further examine the impact of metals upon environmental emissions and to assist in developing and refining regulatory strategies for dealing with such an impact. (3)

The research was designed to identify:

- the distribution of metal emissions among ash, scrubber blowdown water, flue gas particulate and flue gas vapor
- the sensitivity of metal fate to RKS operating conditions
- the dependence of metal emissions on chlorine content of the incinerated organic waste.

This testing was conducted in conjunction with the development of a metal partitioning model under a U.S EPA contract with EERC Corporation; data from these tests will be used in part to evaluate the predictive capability of the model.

APPROACH

As indicated in Figure 1, the RKS consists of a rotary kiln primary combustion chamber followed by an afterburner. Combustion gases exiting the afterburner are quenched after which they enter a primary air pollution control system. This system consists of a venturi scrubber and packed column scrubber, and is followed by secondary air pollution control consisting of a carbon bed adsorber and a high efficiency particulate filter.

The feed material consisted of synthetic waste formulations mixed into a clay absorbent material. In a four-week series of eight parametric tests, aqueous mixtures were spiked into the solid material, which was then screw-fed to the RKS.

The tests examined the fate of the hazardous constituent trace elements arsenic (As), lead (Pb), cadmium (Cd), chromium (Cr), and barium (Ba). In addition, the non-hazardous elements, copper (Cu), magnesium (Mg), bismuth (Bi), and strontium (Sr) were spiked into the test feed to establish whether their discharge distributions were comparable to those for the hazardous elements.

The feed concentrations of metals are presented in Table 1.

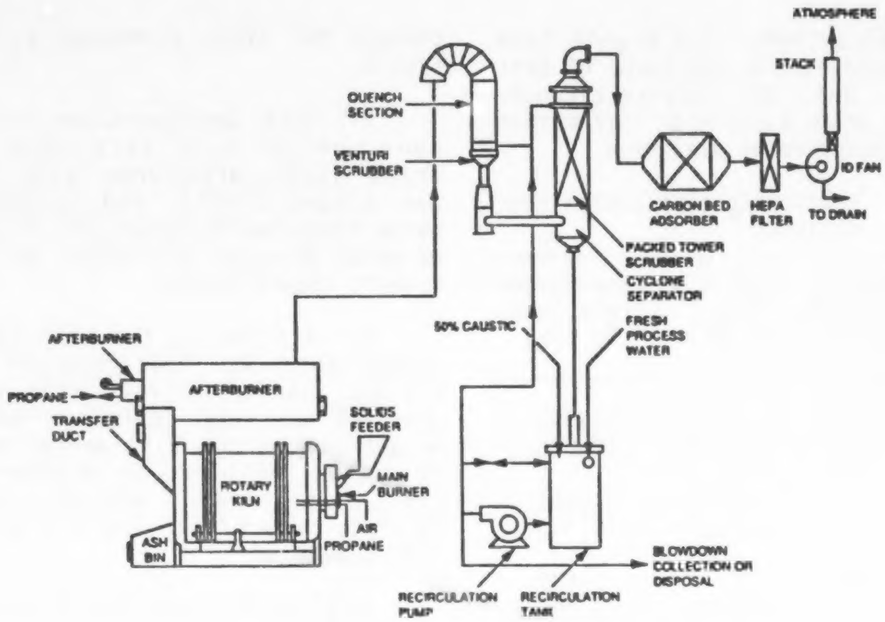
ATMOSPHERE
STACK
QUENCH SECTION
VENTURI SCRUBBER
ID FAN
CARBON BED ADSORBER
HEPA FILTER
TO DRAIN
PACKED TOWER SCRUBBER
CYCLONE SEPARATOR
50% CAUSTIC
FRESH PROCESS WATER
AFTERBURNER
PROPANE
AFTERBURNER
TRANSFER DUCT
SOLIDS FEEDER
ROTARY KILN
MAIN BURNER
AIR
PROPANE
ASH BIN
BLOWDOWN COLLECTION OR DISPOSAL
RECIRCULATION PUMP
RECIRCULATION TANK

Figure 1. Schematic of the CRF Rotary Kiln System

Table 1. Nominal feed metal concentrations.[a]

Metal	Concentration (ppm)
Arsenic	50
Barium	50
Bismuth	180
Cadmium	10
Chromium	90
Copper	500
Lead	50
Magnesium	17,000
Strontium	300

[a] Based on average clay matrix metals concentrations of: Bi (12 ppm); Cr (53 ppm); Pb (3 ppm); Mg (2.2 percent); Sr (34 ppm)

These values represent the sum of metals in the spike solution and background levels of metals in the feed clay. In addition to the metals, toluene, chlorobenzene, and tetrachloroethylene were added to the solid material in predetermined amounts to achieve the necessary chlorine levels and heat content in the feed.

Kiln temperature, afterburner temperature and the chlorine content of the organic liquid were varied based on a factorial experimental design for three variables over three levels.

The target conditions for the three variables covered the following ranges: feed liquid matrix chlorine content (0 to 8 percent); kiln temperature (816° to 927°C [1500° to 1700°F]); and afterburner temperature (982° to 1204°C [1800° to 2200°F]). Table 2 gives the values for each of the test variables for seven test points specified by the factorial design algorithm. The eighth test point represents a duplicate of test point 4. This duplicate test condition was added to provide information on test measurement precision.

Table 2. Parametric test design conditions.

Test	Feed Cl Content (wt %)	Kiln Exit Temp, ^oC (^oF)	Afterburner Exit Temp, ^oC (^oF)
1	0	871 (1,600)	1,093 (2,000)
2	4	816 (1,500)	1,093 (2,000)
3	4	927 (1,700)	1,093 (2,000)
4	4	871 (1,600)	1,093 (2,000)
5	4	871 (1,600)	1,204 (2,200)
6	4	871 (1,600)	982 (1,800)
7	8	871 (1,600)	1,093 (2,000)
8[a]	4	871 (1,600)	1,093 (2,000)

[a] Test 8 is a duplicate of test 4 .

Actual test conditions achieved were very close to target test conditions for all test points except point 2. The average afterburner exit temperature was approximately 22°C lower than the target temperature of 1093°C for this test. For all other parametric tests, average actual operating temperatures were within 10°C of target conditions.

Actual feed chlorine content was 0 percent for test 1; 8.3 percent for test 7; and ranged from 3.4 to 4.6 percent for tests 2 through 6, and test 8.

All tests were conducted at the same nominal kiln exit flue gas oxygen (12%), afterburner exit flue gas oxygen (7.5%), and synthetic waste feedrate (63 kg/hr [140 lb/hr]), of which 18 kg/hr (40 lb/hr) was the organic liquid matrix.

For all tests, the kiln rotational speed was held constant at 0.2 rpm, and the primary APCDs were operated at the following nominal settings: scrubber blowdown rate (2 L/min); venturi liquid flowrate (75 L/min); venturi pressure drop (6 kPa); packed tower liquid flowrate (110 L/min).

Sampling for each test included:

- a composite sample of all feed material (clay/organic liquid mixture just before kiln introduction, and aqueous metal spike solution)
- samples of scrubber blowdown water over time
- composite samples of kiln ash from each test
- samples of the flue gas at the afterburner and scrubber exits for metal capture in the particulate and backup impinger train
- samples of the flue gas at the afterburner and scrubber exits for volatile organic hazardous constituents. (2)

RESULTS

Table 3 represents a summary of metal discharge distribution data collected during the eight parametric tests.

Metal Volatility

Metals exiting the kiln followed

Table 3. Normalized metal discharge distributions (% of total measured).

Test Number:	2	4	8	3	6	4	8	5
Primary Variable:	Kiln Exit Temperature (^{o}C)				Afterburner Temperature (^{o}C)			
Target Value:	816	871	871	927	982	1093	1093	1204
Test Average:	825	875	876	927	984	1088	1093	1196
Constants 1;2:	Afterburner=1093^{o}C; Cl=4%				Kiln= 871^{o}C; Cl=4%			
Const. 1 Avg.:	1071	1088	1093	1092	875	878	873	871
Const. 2 Avg.:	3.7	3.8	4.6	4.2	3.4	3.8	4.6	3.6
Arsenic								
Kiln Ash	94.4	86.1	92.3	84.0	93.6	86.1	92.3	91.2
Scrub.Ex. Gas	2.1-2.9	3.8-5.8	2.3-4.1	6.8-8.4	2.6-3.8	3.8-5.8	2.3-4.1	3.0-4.3
Scrub. Water	2.7	8.2	3.6	7.6	2.6	8.2	3.6	4.6
Barium								
Kiln Ash	74.3	79.6	69.9	69.6	85.2	79.6	69.9	86.9
Scrub.Ex. Gas	3.8	2.2	5.5	1.6	2.2	2.2	5.5	1.6
Scrub. Water	21.9	18.2	24.7	28.8	12.5	18.2	24.7	11.5
Bismuth								
Kiln Ash	25.8	22.2	30.0	22.9	20.9	22.2	30.0	30.1
Scrub.Ex. Gas	41.5	41.1	35.2	50.7	47.4	41.1	35.2	37.1
Scrub. Water	32.6	36.7	34.7	26.3	31.6	36.7	34.7	32.8
Cadmium								
Kiln Ash	<15.2	<10.3	<12.9	<10.7	<13.9	<10.3	<12.9	<14.5
Scrub.Ex. Gas	43-49	56-61	42-45	62-69	61-69	56-61	42-45	55-62
Scrub. Water	42-51	34-39	45-55	27-31	25-31	34-39	45-55	31-38
Chromium								
Kiln Ash	94.7	94.1	85.9	95.3	95.5	94.1	85.9	89.3
Scrub.Ex. Gas	3.0	2.0	1.9	2.1	1.1	2.0	1.9	4.2
Scrub. Water	2.3	3.9	12.2	2.6	3.4	3.9	12.2	6.6
Copper								
Kiln Ash	84.2	75.8	76.2	82.3	79.2	75.8	76.2	75.1
Scrub.Ex. Gas	12.9	15.1	17.8	14.1	15.2	15.1	17.8	16.0
Scrub. Water	3.0	9.1	5.9	3.6	5.6	9.1	5.9	8.9
Lead								
Kiln Ash	12.6	15.0	13.7	10.4	5.8	15.0	13.7	13.8
Scrub.Ex. Gas	50.4	48.9	50.2	67.2	60.6	48.9	50.2	45.0
Scrub. Water	37.0	36.1	36.0	22.4	33.6	36.1	36.0	41.1
Magnesium								
Kiln Ash	99.4	99.3	99.3	99.5	99.3	99.3	99.3	99.2
Scrub.Ex. Gas	0.2	0.1	0.2	0.1	0.1	0.1	0.2	0.1
Scrub. Water	0.4	0.6	0.5	0.4	0.6	0.6	0.5	0.7
Strontium								
Kiln Ash	82.9	93.0	89.8	90.1	94.3	93.0	89.8	81.9
Scrub.Ex. Gas	1.1	1.7	3.5	1.6	1.3	1.7	3.5	3.7
Scrub. Water	16.0	5.3	6.6	8.3	4.4	5.3	6.6	14.4

Table 3. (Cont'd).

Test Number:	1	4	8	7
Primary Variable:	Feed Chlorine Content (wt %)			
Target Value:	0	4	4	8
Test Average:	0	3.8	4.6	8.3
Constants 1;2:	Kiln = 871°C; AB = 1093°C			
Const. 1 Avg.:	872	878	873	871
Const. 2 Avg.:	1094	1088	1093	1092
Arsenic				
Kiln Ash	93.9	86.1	92.3	92.4
Scrub.Ex. Gas	1.7-2.2	3.8-5.8	2.3-4.1	4.0-4.8
Scrub. Water	3.9	8.2	3.6	2.7
Barium				
Kiln Ash	68.8	79.6	69.9	78.6
Scrub.Ex. Gas	2.0	2.2	5.5	2.4
Scrub. Water	28.8	18.2	24.7	19.0
Bismuth				
Kiln Ash	64.8	22.2	30.0	36.3
Scrub.Ex. Gas	15.7	41.1	35.2	38.4
Scrub. Water	19.5	36.7	34.7	25.4
Cadmium				
Kiln Ash	<29.3	<10.3	<12.9	<9.3
Scrub.Ex. Gas	42-54	56-61	42-45	68-74
Scrub. Water	29-46	34-39	45-55	68-74
Chromium				
Kiln Ash	95.7	94.1	85.9	92.1
Scrub.Ex. Gas	1.4	2.0	1.9	2.8
Scrub. Water	2.8	3.9	12.2	5.1
Copper				
Kiln Ash	97.6	75.8	76.2	58.0
Scrub.Ex. Gas	0.8	15.1	17.8	33.2
Scrub. Water	1.6	9.1	5.9	8.8
Lead				
Kiln Ash	83.7	15.0	13.7	6.0
Scrub.Ex. Gas	11.6	48.9	50.2	73.6
Scrub. Water	4.7	36.1	36.0	20.3
Magnesium				
Kiln Ash	99.6	99.3	99.3	99.4
Scrub.Ex. Gas	0.03	0.1	0.2	0.1
Scrub. Water	0.36	0.6	0.5	0.5
Strontium				
Kiln Ash	91.8	93.0	89.8	90.7
Scrub.Ex. Gas	2.5	1.7	3.5	1.6
Scrub. Water	5.7	5.3	6.6	7.7

one of three pathways; they either left in the kiln ash, or traveled to the afterburner as fly ash or as volatilized compounds. In this discussion, those metals with a propensity towards partitioning in the kiln ash will be referred to as "refractory" metals, while those which tend to exit from the kiln to the afterburner can be grouped into a category of "volatile" metals. These designations are based on the amount of each metal found in the kiln ash, as a percentage of the total metal measured among the process streams (ash, scrubber blowdown, and flue gas). An assumption in making these distinctions is that metals traveling from the kiln to the afterburner are predominantly the result of volatilization, rather than entrainment in fly ash.

Cadmium, lead, and bismuth appeared to be the most volatile of the nine metals over the range of kiln temperatures tested, with average partitioning to the kiln ash of <15, 20, and 32 percent of the measured amounts for each of the three metals, respectively.

Barium, copper, strontium, arsenic, chromium, and magnesium appeared to be more refractory, with average partitioning of 77, 79, 89, 91, 93, and 99 percent to the kiln ash for each of the metals, respectively.

With the exception of arsenic, the observed order in the degree to which the metals volatilize correlates strongly with that which would be predicted by 'volatility temperatures'(the temperatures at which the vapor pressure of the most volatile principal species of each metal under oxidizing conditions is 10 $^{-6}$ atm). The fact that arsenic is significantly less volatile than expected suggests that either a refractory compound is preferred over the predominant arsenic species (As_2O_3), or that some chemical interaction, such as strong adsorption to the clay, occurred. (4)

Kiln Ash Partitioning

The only metals for which kiln ash partitioning appeared to be affected by changes in kiln temperature were the most volatile metals (cadmium and lead) and arsenic. For these three metals, slight decreases in kiln ash fractions were seen with increasing kiln temperature. Kiln temperature effects for the other individual metals, as well as for total metals, were not significant within data variability.

The effect of increasing feed chlorine content on the partitioning of metals appeared to be much more significant than that of kiln temperature. As kiln and afterburner temperatures were held constant, and feed chlorine content increased from 0.0 to 8.3 percent, the overall fraction of metals partitioning to the kiln ash dropped from 81 to 63 percent.

Chlorine content of the feed affected the volatility of individual metals to different degrees. Kiln ash partitioning of the three volatile metals decreased measurably as chlorine content rose. In the case of bismuth, the fraction of the measured metal found in the kiln ash dropped from 65 to 36 percent as feed chlorine concentration increased from 0.0 to 8.3 percent. Kiln ash fractions of cadmium and lead dropped from 29 to 9 percent, and from 84 to 6 percent, respectively, over the same chlorine range.

Only one of the refractory metals showed an increase in volatility with increasing feed chlorine content. The fraction of measured copper found in the kiln ash dropped from 98 to 58 percent as feed chlorine increased. The volatility of the other refractory metals appeared relatively stable with increasing feed chlorine.

Scrubber Efficiency

The split of metals between scrubber exit gas and scrubber water determines the apparent scrubber efficiency, defined as the ratio of metals in the water to the sum of the metals in the two splits.

Scrubber efficiency for total metals ranged from 33 to 56 percent, and appeared to be negatively impacted by increases in kiln temperature and feed chlorine content.

Average scrubber efficiencies for the individual metals ranged from a low of 32 percent for copper to a high of 88 percent for barium. Average scrubber efficiency for the three volatile metals was lower than that for five of the six refractory metals.

Kiln temperature effects on scrubber efficiency were measurable in the cases of two of the volatile metals. Decreases in scrubber efficiency, from 51 to 31 percent for cadmium and from 42 to 25 percent for lead, were seen with increases in kiln temperature from 825°C to 927°C. This is consistent with the changes in volatilization of these metals experienced with changes in kiln temperature.

The effect of chlorine on scrubber efficiency for individual metals was significant for copper, arsenic, bismuth, and cadmium. In each case, the effect of increasing feed chlorine was to decrease scrubber efficiency. Decreases were as follows: copper (from 67 to 21 percent); arsenic (67 to 38 percent); cadmium (46 to 26 percent); and bismuth (55 to 40 percent).

The effect of afterburner temperature on scrubber efficiency for individual metals was less substantial than that of kiln temperature and feed chlorine content. Modest increases in scrubber efficiency were seen along the increasing afterburner temperature range for bismuth and lead.

Flue Gas Phase Distribution

Standard Method 5 trains were used to collect samples of flue gas particulate- and vapor-phase metals. In this discussion, two assumptions regarding this sampling technique are made: (1) all particulate-phase metals are collected on the filters, and (2) all vapor-phase metals are collected in the impingers; vapor-phase metals do not condense on the filters, nor do they pass through the impingers. (In actuality, the 'vapor-phase' likely includes some water-soluble metal that has wept through the filters and collected in the impingers.)

The distribution of metals in the flue gas favored the particulate phase over vapor. Average particulate phase metals as a fraction of total flue gas metals was highest for the three volatile metals, with lead at 96 percent, cadmium at 90 percent and bismuth at 84 percent. For the refractory metals, the fraction of flue gas metals exiting as particulate ranged from 82 percent for copper to 31 percent for barium.

None of the test variables had a clear effect on the split of total flue gas metals between the two phases. Likewise, effects of test variables on the flue gas phase distribution for the individual metals were not significant within data variability. (4)

CONCLUSIONS

In the subject test series, the trace metals cadmium, lead and bismuth were found to be relatively volatile, while barium, copper, strontium, arsenic, chromium and magnesium were relatively non-volatile.

Average kiln ash partitioning ranged from <15 percent for copper to 99 percent for magnesium. Average scrubber efficiencies for the individual metals ranged from 32 percent for copper to 88 percent for barium.

Both kiln ash partitioning and scrubber efficiency appeared to be impacted negatively by increases in feed chlorine content and, to a lesser extent, increases in kiln temperature.

Average particulate-phase metals as a fraction of total flue gas metals ranged from 31 percent for barium to 96 percent for lead. No clear effects of the three test variables on flue gas phase distributions were apparent.

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

TREATMENT OF RCRA HAZARDOUS/RADIOACTIVE MIXED WASTE

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ABSTRACT

The following paper describes a treatment process for a radioactive/chemical mixed waste sludge. The waste, which was generated during remedial action under the Department of Energy's (DOE) Formerly Utilized Sites Remedial Action Program (FUSRAP), was designated as mixed because of its uranium content (up to 14,000 picoCuries per gram) and the presence of chemical constituents which caused the waste material to fail the Resource Conservation and Recovery Act (RCRA) characteristic test for ignitability.

Because the sludge was classified as a mixed waste, no commercial or federal facilities were able to dispose of the material. As a result, various alternatives were proposed to either eliminate the chemical constituents which contributed to the ignitability characteristic or to separate the waste into a RCRA hazardous waste and a low-level radioactive waste. Based on an evaluation of technical feasibility, regulatory requirements, and cost, a thermal treatment process was selected to eliminate the ignitability characteristic and allow for disposal as a low-level radioactive waste. The treatment process was accomplished in two phases, the lengths of which were determined during bench scale testing. Phase I consisted of heating the waste slowly to a maximum temperature of 180^{o}F. This phase was implemented to drive off the highly volatile compounds which contributed to the ignitability characteristic and to ensure that ignition of the material did not occur. During Phase II of the process, the temperature was substantially increased to further reduce the concentration of the contained organic compounds. Each phase utilized a ventilation system designed to contain organic chemicals and radioactive particulates. The system contained sample ports which were used for both health and safety and process efficiency monitoring.

After the treatment was completed, the moisture content was typically reduced from approximately 70 percent to about 20 percent. The moisture content was further reduced for ultimate disposal by mixing with diatomaceous earth in a 1:1 ratio by volume. Laboratory results from the analysis of the treated sludge indicated substantial reductions in the concentrations of volatile and semi-volatile organic compounds as well as the elimination of the RCRA characteristic of ignitability. The waste has now been transported and disposed of as a low-level radioactive waste at a DOE facility.

INTRODUCTION

Under the Department of Energy's (DOE) Formerly Utilized Sites Remedial Action Program (FUSRAP), Bechtel National, Inc. performed remedial actions to clean up radioactive materials at the National Guard Armory (NGA) in Chicago, Illinois. These radioactive materials resulted from uranium processing operations during the early years of the nation's atomic energy program.

The remedial actions at the NGA generated sixteen 55-gallon drums of sludge. This sludge came from catch basins and drain lines in the motor pool area of the armory. The sludge contained uranium concentrations up to 14,000 picoCuries/gram (pCi/g) and elevated levels of lead. In addition, the sludge contained a variety of organic volatile and semi-volatile compounds such as benzene, toluene, xylene, dichloroethane, trichloroethane, and phenol. Samples were collected from each drum by using a one inch diameter, 36 inch long vertical sampling device. Multiple vertical samples from a drum were blended together to create a single sample from each respective drum. Samples were analyzed by the appropriate Environmental Protection Agency (EPA) approved methods. Volatile organic and semi-volatile organic analyses were performed by Gas Chromatography/Mass Spectroscopy (GC/MS) by EPA methods 8420 and 8250, respectively. Metal analyses were conducted by Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICPAES), EPA Method 6010. The organic and lead constituents present in the sludge were probably the result of NGA vehicle maintenance operations.

Laboratory analysis of the sludge indicated a flashpoint of <70°F and consequently it met the Resource Conservation and Recovery Act (RCRA) definition for the characteristic of ignitability (Ref. 1). All RCRA characteristeric analyses were perfromed by methods as defined by EPA. This RCRA characteristic and the concentrations of uranium present in the sludge resulted in a mixed waste classification.

PURPOSE

Because of a lack of treatment, storage, or disposal facilities for mixed waste, a treatment scheme had to be developed to eliminate either the ignitability or the radioactive characteristics from the sludge or to separate the material into two distinct wastes, a RCRA hazardous waste and a low-level radioactive waste.

APPROACH

Several treatment and disposal options for the sludge were explored. These included disposal at a government low-level radioactive waste disposal site, incineration at both a government-owned and at a commercial hazardous waste incinerator, treatment by new technologies such as supercritical water oxidation and a microwave technique, chemical treatment to separate the uranium from the sludge, and a thermal treatment process to reduce the concentrations of organics and thus, raise the flashpoint to eliminate the ignitability characteristic.

The thermal treatment option was chosen as the method for field operations. Bench scale tests using the thermal treatment method proved very successful. These tests resulted in the flashpoint of the sludge being raised from the initial <70^{o}F to greater than 800^{o}F. In addition to eliminating the RCRA ignitability characteristic, a volume reduction in the total amount of waste was observed. The primary reason for the volume reduction was the moisture content of the sludge being decreased from about 70% moisture to less than 20% moisture. The other alternatives were eliminated due to cost, technical feasibility, or regulatory restrictions.

Before preparing for field operations, several safety concerns were addressed. The primary concern was the ignition of the sludge during processing. The bench tests had shown if heat was not evenly distributed, the sludge would form red embers, and the potential for fire was increased. Other health concerns were worker protection from dust particles that contained radioactive or lead particulates and from benzene gases. The formation of a crust on the top of the sludge was also of concern since this would cause gases to accumulate in the drum, therefore, resulting in a potentially explosive condition.

The system which was designed for field operations was kept as simple as possible while addressing all safety and operating concerns. Ventilation systems were designed to meet capture velocity and flow rate requirements of the American Conference of Governmental Industrial Hygienists (ACGIH) and the National Fire Protection Association (NFPA), respectively (Refs. 2, 3). Off-the-shelf items were used where feasible.

Field processing of the waste sludge was divided into two phases. Phase I of the operation included heating the sludge in the original 55-gallon drums in a controlled manner to drive off the majority of the organic volatile compounds and to reduce the potential for fire and explosion. Bench tests had shown that the temperature should not be increased above 180^{o}F in Phase I because of the potential for fire. Commercially available drum heaters that were thermostatically controlled with a 35^{o}F/hour temperature increase capacity were utilized. The ventilation system used in Phase I was a low volume, high negative pressure system powered by a 200-cubic feet/minute (cfm), 105-inches of water suction, high efficiency particulate air (HEPA) filter vacuum. This ventilation system used two activated carbon filter beds in series between the drums of sludge being treated and the vacuum. The carbon filters adsorbed organic vapors that were generated during the processing and the HEPA filter captured radioactive and metal particulates that were emitted. To prevent the sludge from forming a crust and therefore accumulating organic gases, a commercial concrete vibrator was used to continuously agitate the waste. This also aided in the liberation of organic gases. Sample ports were provided in the system design to allow for monitoring of the process efficiency and for health and safety concerns. Phase I continued until field flammability tests were negative and organic vapor analyzer (OVA) readings had decreased to 10% of initial readings. The total time for the completion of Phase I of the process was approximately 8 hours per drum. A schematic of the Phase I system is shown in Figure 1.

Phase II of the thermal treatment operation involved heating the sludge to the highest temperature attainable with the drum heaters to further reduce the moisture content and to continue to reduce the organic volatile and semi-volatile concentrations. The Phase II ventilation system was also designed with sampling ports for monitoring activities. This system included the use of fume hoods suspended from a mobile gantry crane that were connected to a 2000-cfm HEPA blower unit with an activated carbon filter in the ventilation line. The gantry crane was used to eliminate the need for personnel to handle hot drums. Once Phase II treatment had progressed to the point that the moisture content had been reduced to approximately 20%, the treated sludge was further stabilized with diatomaceous earth in a 1:1 ratio by volume. This was done to ensure the sludge met moisture content requirements for disposal at a low-level radioactive disposal site. Phase II of the operation required an average of 4 hours per drum. The layout of the Phase II system is shown in Figure 2.

RESULTS

Once all processing was complete, including stabilization with diatomaceous earth, a total of fourteen 55-gallon drums of treated waste remained. The treatment process yielded more than a 50% reduction in volume before the sludge was stabilized with the diatomaceous earth.

Laboratory analysis of the treated sludge has confirmed that it no longer demonstrates the RCRA characteristic of ignitability. Monitoring during process operations confirmed the efficiency of the treatment system in removing organics from the sludge while protecting the work environment from the release of organic vapors and airborne particulate hazards. Table 1 shows typical reductions in volatile and semi-volatile concentrations after treatment. This thermal treatment process proved to be a success as the waste can now be treated as a low-level radioactive waste for the purposes of disposal.

The total cost of this operation was about $190/gallon of treated waste. This cost includes all capital equipment, labor, and other incidental costs. Because the capital equipment could be reused in additional processing of waste, the total cost would decrease with increasing volumes of waste. The cost would be reduced to about $65/gallon for 6000 gallons of waste and about $55/gallon for 20,000 gallons of waste. The breakdown of the final cost of the 880 gallons of treated waste was approximately $95/gallon for capital equipment, $65/gallon for labor, and $30/gallon other costs. Labor included a site health and safety officer, operations superintendent, 3 support laborers, and engineering support in the home office.

CONCLUSIONS

Based on the experience from this operation, a system of this type would be applicable in many similar situations, especially to small quantity generators.

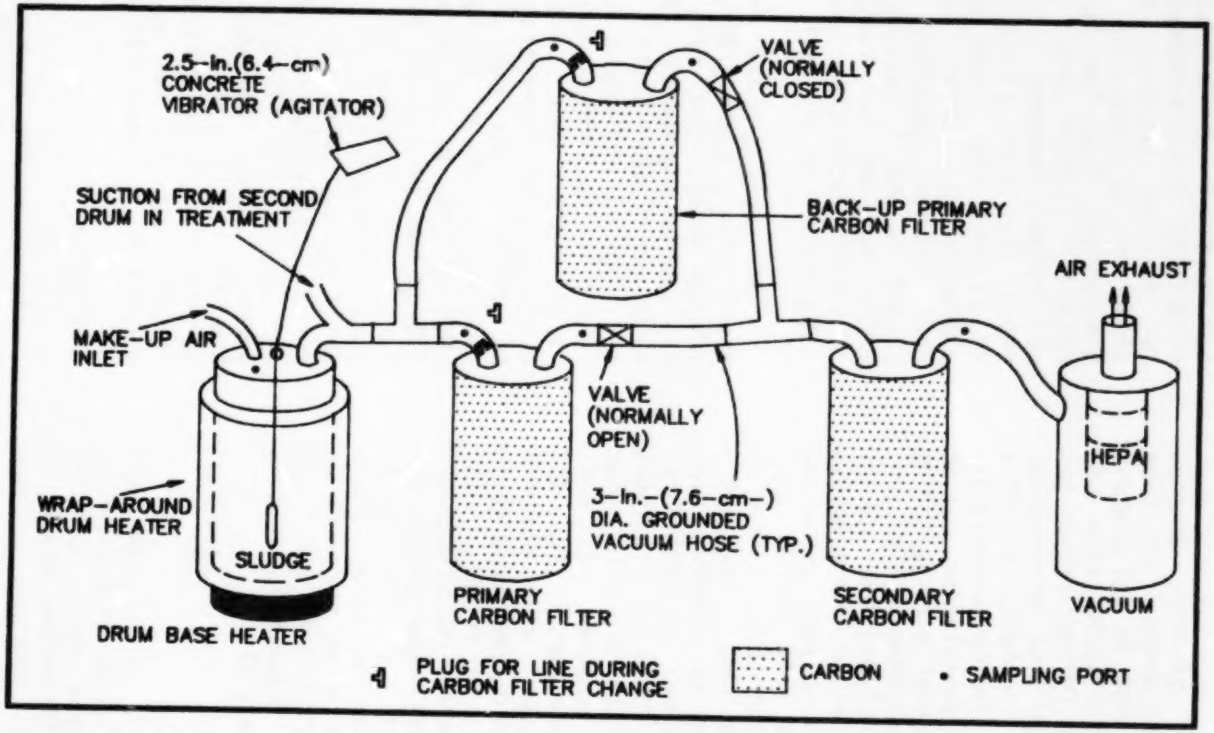
2.5-In.(6.4-cm) CONCRETE VIBRATOR (AGITATOR)
SUCTION FROM SECOND DRUM IN TREATMENT
MAKE-UP AIR INLET
WRAP-AROUND DRUM HEATER
SLUDGE
DRUM BASE HEATER
PRIMARY CARBON FILTER
VALVE (NORMALLY OPEN)
3-In.-(7.6-cm-) DIA. GROUNDED VACUUM HOSE (TYP.)
VALVE (NORMALLY CLOSED)
BACK-UP PRIMARY CARBON FILTER
SECONDARY CARBON FILTER
AIR EXHAUST
HEPA
VACUUM
PLUG FOR LINE DURING CARBON FILTER CHANGE
CARBON
• SAMPLING PORT

FIGURE 1 PHASE I SLUDGE TREATMENT EQUIPMENT CONFIGURATION

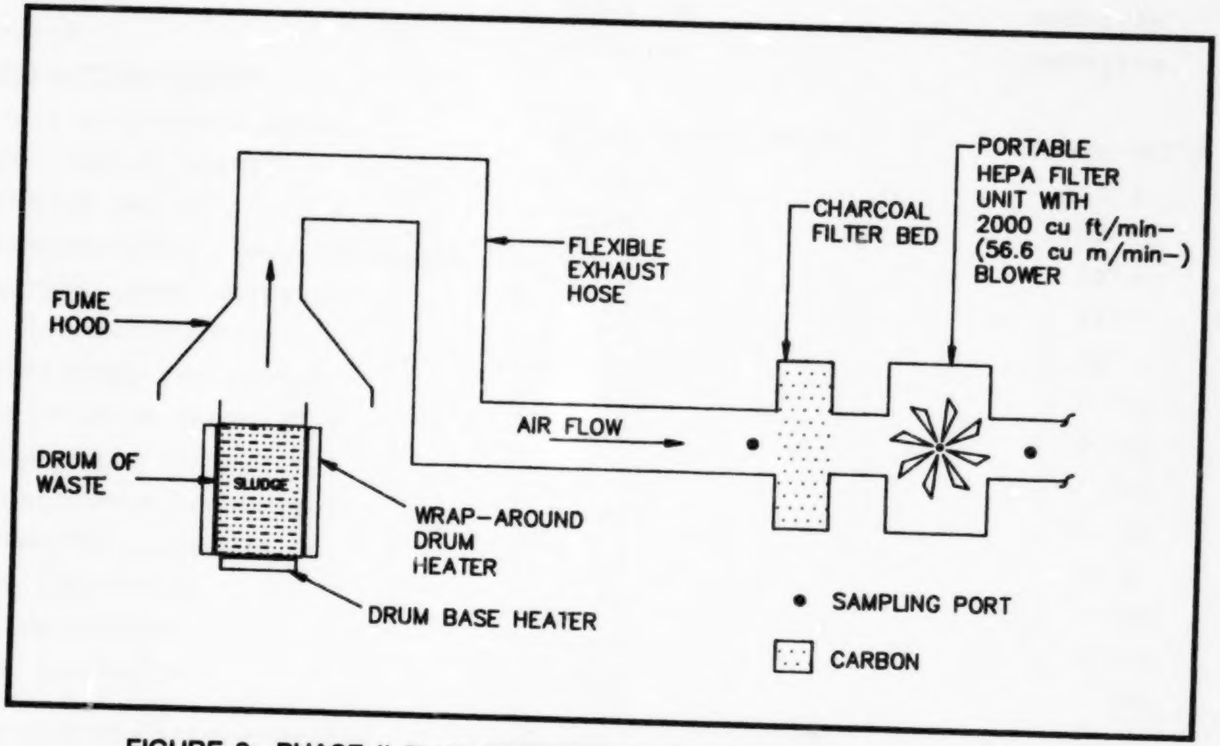
FUME HOOD
DRUM OF WASTE
SLUDGE
FLEXIBLE EXHAUST HOSE
AIR FLOW
WRAP-AROUND DRUM HEATER
DRUM BASE HEATER
CHARCOAL FILTER BED
PORTABLE HEPA FILTER UNIT WITH 2000 cu ft/min- (56.6 cu m/min-) BLOWER
• SAMPLING PORT
▨ CARBON

FIGURE 2 PHASE II SLUDGE TREATMENT EQUIPMENT CONFIGURATION

TABLE 1
SUMMARY OF CONTAMINANT CONCENTRATIONS IN NGA SLUDGES BEFORE AND AFTER TREATMENT

CONTAMINANT (CLASSIFICATION)	BEFORE TREATMENT AVERAGE CONCENTRATION (MG/KG)	AFTER TREATMENT AVERAGE CONCENTRATION (MG/KG)
Toluene (volatile)	165	.26
Xylene (volatile)	542	< .25
Benzene (volatile)	15	.73
Ethylbenzene (volatile)	88	1.0
Trichloroethane (volatile)	82	< .25
Dichloroethane (volatile)	7	< .25
Trichloroethene (volatile)	5	< .25
Dichloroethene (volatile)	14	< .25
Phenol (semi-volatile)	3	< 20
Naphthalene (semi-volatile)	197	22
Methylnaphthalene (semi-volatile)	338	36.2
Lead (heavy metal)	1260	1460
Chromium (heavy metal)	116	123.1
Uranium-238 (radioisotope)	14000 pCi/g (max)	14000 pCi/g (max)
RCRA CHARACTERISTICS:		
Reactivity:	negative	negative
Corrosivity:	negative	negative
EP Toxicity:	negative	negative
Ignitability:	ignitable (flashpoint < 70°F)	negative

Caution must be exercised, however, in utilizing this type of system with regard to the concentration of organics. The waste should be proven to be only flammable and not explosive, the filter media should have a high affinity for the contaminants, and the effectiveness of the system should be demonstrated prior to field use.

In addition, the appropriate regulatory agencies must be involved in plans for treatment and disposal of the waste from the outset to ensure that the treatment will result in the required reclassification of the waste. The success of the thermal treatment in converting the mixed waste at the NGA to a low-level radioactive waste offers one reliable solution to a problem for which few alternative solutions currently exist.

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OPERATING EXPERIENCES OF THE EPA MOBILE INCINERATION SYSTEM WITH VARIOUS FEED MATERIALS

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ABSTRACT

During the past four years, the USEPA's Mobile Incineration System (MIS) has processed a wide variety of feeds. Besides incinerating the hazardous materials for which the MIS was designed, the unit has incinerated contaminated debris including wood pallets, steel and fiber drums, and plastics. This paper identifies significant physical and chemical characteristics of various feed materials and their relationship to MIS performance. The effects of these feed characteristics on specific MIS components are correlated. Several problem characteristics have been mitigated by corrective actions. The operating experience with the MIS has provided valuable data on the limits of its incineration capacity as well as reliability of the unit in relation to various feedstocks. The information contained in this paper is directly applicable to field use of mobile and transportable incinerators at Superfund and other industrial cleanup sites.

INTRODUCTION

Under the sponsorship of the Office of Research and Development of the U.S. Environmental Protection Agency (EPA), the Mobile Incineration System (MIS) was designed and constructed to demonstrate high-temperature incineration of hazardous wastes (1). The system essentially consists of a refractory-lined rotary kiln, a secondary combustion chamber (SCC), and an air pollution control system.

These three components are mounted on three separate heavy-duty semitrailers. Monitoring equipment is carried by a fourth trailer.

Over the lifetime of the MIS, a wide variety of feed materials have been processed (2,3). These materials exhibited differences in characteristics that affected the MIS in various ways. Often a particular characteristic or a combination of characteristics would affect the MIS performance adversely. The experiences gained from field operations of the MIS during the past four years have increased the understanding of the interplay of feed characteristics with hardware.

This paper describes the effects of feed characteristics on the MIS performance; correlates various feed characteristics with affected parts of the system; describes actions taken to mitigate the resulting problems; and discusses the limits imposed on capacity and reliability by the various feed characteristics.

FEED CHARACTERISTICS

Both the physical and the chemical properties of the feed determine incineration system performance (4). Important physical properties include: heating value, morphology, density, rheology, ash particle-size distribution, and fusion characteristics. Important chemical properties include the composition of the feed as shown by: organic content,organic hazardous constituents, acid forming elements such as sulfur and the halogens, moisture content, and inorganic ash components. These properties can affect the operating parameters, the capacity, and the reliability of the incineration system. Many of these properties are interdependent as far as their effect on the incinerator performance. The manner in which these properties affect the performance of incineration systems, based on the experience of the MIS, is summarized in Table 1.

EFFECT OF HEATING VALUE

Heating value of the feed material affects both feed capacity and fuel usage of the incinerator. An increased heating value of feed material can raise kiln temperature, which can become uncontrollable. The kiln then requires greater amounts of oxidant to complete combustion and greater quantities of inert material to control kiln temperature. The temperature increase can limit feed capacity. The MIS reached its capacity limit at 1.33 to 1.61 megawatts (MW) heat input to the kiln. Feed materials such as plastics, trash, wooden pallets, and brominated sludge had capacity constraints caused by high calorific values. Maximum feed capacities for these materials ranged from 90 kg/hr for pure plastics to 859 kg/hr for brominated sludge as shown in Table 2.

Solid materials with high calorific values cause transient behaviors that sometimes further limit feed capacity. Plastics, trash, and wood ignite almost immediately after they are fed to the kiln. Gases evolved from these materials burn rapidly producing a sharp increase in kiln temperature and a sharp decrease in excess oxygen.

Prior to system modifications implemented in 1987, the MIS was extremely sensitive to these transient behaviors, which caused many feed stoppages. After the addition of the LINDE^R Oxygen Combustion System (OCS),the MIS response to the transient behaviors was improved, and feed stoppages due to low oxygen were virtually eliminated (5). However, there were still many feed cutoffs caused by excessive kiln temperatures. These were minimized by operating the kiln at the lower end (790°C) of the temperature range allowed by the RCRA permit, and by using water injection to control kiln temperatures.

For brominated sludge, the behavior of the MIS was somewhat different. Large oscillations of the kiln temperature and excess oxygen levels occurred even when the kiln was operated at 790°C. The resulting overtemperatures (greater than 1040°C) caused feed cutoffs and loss of the kiln burners. Loss of the burners increased the length of the feed cutoff period. The operating changes required to alleviate this phenomenon are described below.

TABLE 1. PROPERTIES AFFECTING INCINERATION SYSTEM PERFORMANCE

Property	Hardware affected	Operating parameter affected	Effect on performance	Feeds of concern
Heating value	Rotary kiln	Rotary kiln temperature, Flue gas residence time in SCC	Feed capacity, Fuel usage	Plastics, Trash, Wooden Brominated sludge
Morphology	Feed system, Ash gates		Feed interruptions	Steel rings, Wooden pallets,
Density	Rotary kiln, Corbel	Weight of material held by kiln	Feed capacity	Vermiculite
Rheology	Feed system, Rotary kiln	Frequency of feeding, Ash purity, Kiln rotation speed	Feed capacity	Brominated sludge
Halogen and sulfur content	Quench system, Air pollution control equipment design and operation	Pump cavitation, pH control, Blowdown rate, Particulate emissions	Feed capacity, Caustic usage	Trial burn mixture, Brominated sludge
Moisture	Feed system, SCC	Flue gas residence time in SCC, Rotary kiln temperature	Feed capacity, Fuel usage	Muddy soil, Brominated sludge
Particle size distribution	Cyclone, SCC, Ducts, Wet Electrostatic Precipitator (WEP), Instrumentation	Kiln draft, Particulate emissions Excess oxygen control, Temperature Control	Fouling of ducts, cyclone, SCC, process water system, & Instruments	Erwin Farm soil, Brominated sludge, Vermiculite
Ash fusion characteristics (Determined by chemical characteristics, e.g. alkalis)	Rotary kiln, Cyclone, Ducts, Quench elbow, Instrumentation	Kiln draft, Temperature, Excess O_2 control	Slagging of kiln, Plugging of instruments & downstream equipment	Plastics, Trash Brominated sludge

TABLE 2. FEED CHARACTERISTICS AND EFFECT OF VARIOUS FEEDS ON MIS PERFORMANCE

Feed material	% of Particles <100 microns (Ash)	Heating value (cal/g)	% Moisture	Organic content (%)	Halogen content (%)	Kiln temp. (^oC)	Maximum feed rate (kg/hr)	Limitation on feed	Operating concerns
Denney Farm soil-clay (1985-1986 before mods) 1.24 g/cc density	4.8	47	20	2.5	0.13	871-927	900	SCC res. time, Ram capacity	Jamming of Ram, 3-day req. every 20 days
(1987-1988 after mods)	"	"	"	"	"	788-815	2275 dry corbel	Overflow of kiln	
Mud + Soil	"	"	>70	"	"	"	1140 mud	Doctor blade jamming	
Mud + Plastics	"	1500	"	"	"	"	680	Doctor blade, Kiln	3-day kiln cleanout
								Slagging, Kiln temp. BTU input	cleanout every 10 days
Erwin Farm soil-silt (1985-1986 before mods)	33.4		20			871-927	900	SCC res. time, Ram capacity	Jamming of ram, 3-day SCC cleanout every 5 days
(1987-1988 after mods)	"	"	"	"	"	788-815	2275 dry	Overflow of kiln corbel	
Mud + Soil	"	"	>70	"	"	"	1140 mud	Doctor blade jamming	
Mud + Plastics	"	1500	"	"	"	"	680	Doctor blade, Kiln Slagging, Kiln temp. BTU input	3-day kiln cleanout every 10 days
Plastics & trash	0	3600-10500	0-10	50-100	0-57	788-815	90-320	Doctor blade jamming	3-day
0.9-2.2 g/cc								Kiln slagging, Kiln temp., BTU input	cleanout every 10 days
Wooden pallets 0.5-0.8 g/cc	0	3500	20	80	0	900-925	325	Kiln temp., BTU input	Cut into small pieces

(continued)

TABLE 2 (continued)

Feed material	% of Particles <100 microns (Ash)	Heating value (cal/g)	% Moisture	Organic content (%)	Halogen content (%)	Kiln temp. (^{o}C)	Maximum feed rate (kg/hr)	Limitation on feed	Operating concerns
Steel barrels	0	0	0	0	0	788-815	82-125	Shredder capability	Dull teeth causes balling and ash gate jamming
Vermiculite	0	0	--	0	0	788-815	364	Ram capacity	
Brominated sludge	86	1470-3400	35-42	15-34	1	900-1035	370-859	Kiln temp., Solids residence time, BTU input.	3-day system clean-out every 12 days, fouling of duct-work between Kiln and SCC, fouling of instrumentation, draft control
Trial burn mixture									
Solids	--	190	19.8	4-5	2.6	800-910	1675-1840	Quench system pump Cavitation at 114 kg/hr organic chloride input	Quench system instability, process water TDS
Liquids	NA	3980-4180	0	100	19.6	" "	66-160		

To reduce the amplitude of the temperature excursions, an automatic feed cutoff was introduced into the kiln control system. This stopped feed whenever the kiln temperature exceeded 945°C or the oxygen level dropped below 4% (wet). This action minimized over-temperature incidents, but the oscillation frequency was still large. About four oscillations occurred per hour. Feed was cut off for approximately eight minutes during each oscillation. Feed rate was limited to 450 kg/hr under these operating conditions.

Observations of the kiln during the oscillations showed that the sludge was not igniting rapidly. Several batches of sludge would be fed by the ram before ignition occurred. After ignition, flame would fill the kiln,and oxygen flow and temperature would increase rapidly. After the sludge had burned several minutes, the flames would extinguish, and the oxygen flow and temperature would decrease rapidly to complete the cycle of oscillation. It became apparent that steady ignition of the material was required to prevent the oscillations.

The kiln temperature was increased from 790°C to900°C to provide the necessary energy to evaporate the water and volatile organics so that ignition could be sustained. This operating change was successful, and maximum feed rate was increased to 900 kg/hr by the above changes.

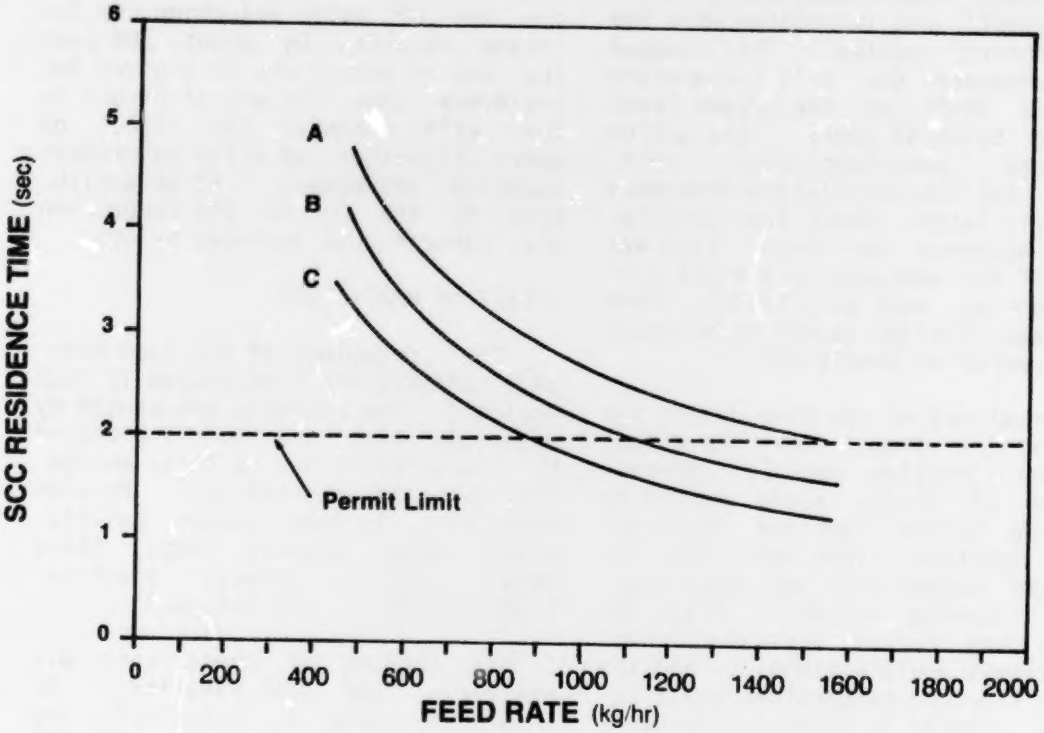
For feeds with high heat content such as brominated sludge, the capacity of the MIS is increased by water injection. Due to its high heat capacity, water provides a very effective heat sink. Consequently, when it is used to control kiln temperature, moisture increases the SCC residence time as compared to the use of excess air. Fig. 1 shows that the use of water injection can increase capacity by about 20% over the use of excess air at a given SCC residence time. The use of oxygen in the kiln enhances the effect of water injection by allowing further capacity increases. At an enrichment to 40% O_2 in the combustion air, capacity can increase by 60%.

EFFECT OF MORPHOLOGY

The morphology of the feed material affects the feed system in that periodic jams usually are caused by materials that are poorly prepared by the shredder due to their morphological characteristics. Problem materials include wooden pallets, metal drum closure rings, thick metal pieces (pipe), plastics, trash, clothing, and mud (6,7).

The feeding of these materials restricts the MIS capacity. As shown in Table 2, relatively dry soils can be fed at rates up to 2275 kg/hr, but the presence of plastics and mud reduces the feed rate to 680 kg/hr.

The shredder is used to prepare the solid feed materials for incineration. For most materials, the shredder works extremely well. However, wooden pallets and metal drum closure rings often cause feed blockages when shredded in the present equipment. While the shredder breaks most of the wooden pallet into 5-cm wood chips, an occasional board will position itself to go through the shredder as a 5-cm-wide by 1.3-m-long sliver. The same is true for the drum lid rings. The shredder sometimes drags a ring through, straightening it but not cutting it. In each case, plugging of the conveyor, weigh scale, or ram follows. The



NOTES:

Solid Feed Heating Value	**1.50 Kcal/g**
Kiln Temperature	**925°C**
SCC Temperature	**1200°C**

A – Water injection using 40% oxygen-enriched air for combustion

B – Water injection using air for combustion

C – Air cooled using either air or 40% oxygen-enriched air for combustion

Figure 1. Effect of cooling media on SCC residence time.

best solution has been to manually separate and prepare these feed materials by cutting them into small pieces (about 24 cm in length) prior to shredding.

The shredder also has performed poorly on materials such as plastic, clothing, trash, and mud. These poorly shredded materials often have jammed at the doctor blade or restricting dam that was originally used to level the granular material on the conveyor belt as the belt exits the shredder hopper. The doctor blade worked quite well for granular material, but it created large blockages when materials such as shredded plastic,clothing, trash, metal, or mud were fed. A roller has been installed to replace the doctor blade, and this has reduced the number of jamming incidents.

The addition of a television camera at the top of the main feed conveyor has permitted the quick detection of feed material jams in the weigh scale chute. This allows the operator to take prompt corrective action and has prevented many hours of feed interruption since it has been installed.

Finely granulated material affected the operation of the ram feeder. It would bypass the ram head and collect on the backside. The material on the backside would periodically prevent the ram from fully retracting. A small chain-plug conveyor was installed and timed to convey the bypassed material to the front side of the ram. This solution has worked quite well.

EFFECT OF DENSITY

The density of the feed determines capacity for many feed materials. For feeds of typical densities (1.5 g/cc), such as soils, the maximum feed rate is 2275 kg/hr, obtained at a kiln revolution rate of 1.6 revolutions per minute (rpm), which gives a typical solids residence time of 30 minutes. For low-density materials such as vermiculite (0.096 g/cc), feed rates up to 364 kg/hr are feasible.

EFFECT OF RHEOLOGY

The rheology of the material affects either the feed system or the decontamination behavior. Muddy soils fed to the MIS would form clumps of material,which were caught by the doctor blade; and also would stick to the conveyor belt, weigh scale, and ram trough. The resulting buildup would periodically plug various parts of the feed system thus reducing overall feed rates to about 1140 kg/hr. This is approximately 50% of the maximum rates achievable with dry soils. Addition of vermiculite has eliminated the sticking of the muddy material while adding only a small amount to the throughput weight.

Brominated sludge feed had a tendency to form balls up to 8 cm in diameter. Since the time required for burnout of a sphere is proportional to the square of its diameter, the large balls require a much longer residence time in the kiln for decontamination. At the normal 1.6 rpm kiln speed for soil, small smoking particles would exit the kiln with the kiln ash. This required limiting feed rate to about 450 kg/hr. However, when the residence time of the sludge was increased by reducing the rpm to 0.8, feed rates up to 900 kg/hr were achievable without smoking.

EFFECT OF HALOGEN AND SULFUR CONTENT

Incineration of brominated and chlorinated wastes generate the acid gases hydrogen bromide (HBr) and hydrogen chloride (HCl). These acid gases affect the capacity, the blowdown rates that control total dissolved solids (TDS) in the process water system, and the particulate emissions.

A capacity limit of 115 kg/hr of acid-forming organic chlorides was encountered during the 1987 trial burn (3). The capacity limit was caused by pump cavitation in the quench system, which cools the gases exiting from the SCC to about 95°C. The cavitation reduced the quench water flow rate, which activates the protective instrumentation resulting in cutoff of the feed and shutdown of the burners. This cavitation was produced by excessive chlorinated waste feed rate as follows: The quench water was treated with caustic solution to neutralize acid gases. Reaction between HCl in the combustion gases and sodium hydroxide (NaOH) in the quench sump produced effervescence. The amount of effervescence increased to violent levels as HCl flow rate increased. The violent effervescence reduced the available net positive suction head (NPSH) of the pump, which causes cavitation at very high HCl loads.

High organic chloride loads also affect particulate emissions through the phenomenon of mist carry-over into the stack. The amount of carry-over is determined by both the HCl loading of the flue gas and the TDS of the process water (3).

In tests performed prior to the 1987 trial burn, particulate emissions were found to exceed the allowable emissions (180 mg/dscm) by as much as a factor of three. Analysis of the Method 5 particulate filter cakes showed that over 90% of the particulate was sodium chloride (NaCl) and sodium hydroxide (NaOH). The emissions were brought into compliance after a mist eliminator was installed.

However, data taken during the 1987 trial burn showed that TDS of the process water also affected particulate emissions. As shown in Fig. 2, particulate emissions were proportional to TDS during the trial burn tests. The data shows that operation with TDS at 20,000ppm provides an adequate safety margin to insure that particulate emissions are in compliance at high organic chloride loadings.

EFFECT OF MOISTURE

Moisture content affects incinerator performance and can adversely affect rheological behavior as described above. Depending upon the heat content of the waste, moisture can either improve or impede incinerator performance.

When using feeds with high heat content, moisture acts as a heat sink to control kiln temperatures.

Conversely, when using feeds with low heat content, moisture increases auxiliary fuel requirements and decreases SCC residence time. Feed rate must be decreased to maintain SCC residence time. The effect of moisture on SCC residence time is shown in Fig. 3.

EFFECT OF PARTICLE SIZE DISTRIBUTION

The particle size distribution of the ash generated from the waste determines the amount of particulate carry-over from the rotary kiln to the rest of the system. The importance of this characteristic can be demonstrated by the MIS experience with Denney Farm soil and Erwin Farm soil. As shown in Table 2, Denney Farm soil is much coarser than the Erwin Farm soil. Up to 25% of the Erwin Farm soil would carry over from the kiln to the SCC. This caused a rapid buildup of solids in the SCC. The solids buildup necessitated a 70-hr shutdown for removal of the slag after each 96 to 120 hours of operation (45,000 kg of soil processed). The behavior of the silt caused the unit to be unavailable for operation an average of 40% of the time due to the need to clean out the SCC. On the other hand, the unit could process the coarser Denney Farm soil for about 600 hours (270,000 kg of soil processed)before a shutdown for slag removal from the SCC was required. The unit was unavailable for 10% of the time due to SCC cleanouts with the coarser Denney Farm soil. In both cases, the buildup of solids in the SCC significantly reduced the availability of the incinerator.

The problem was mitigated in 1987 when a cyclone was added between the kiln and the SCC to remove the fines carried over from the kiln. The system operated over a three-month period and processed over 500,000 kg of solid material without requiring a shutdown for slag removal from the SCC.

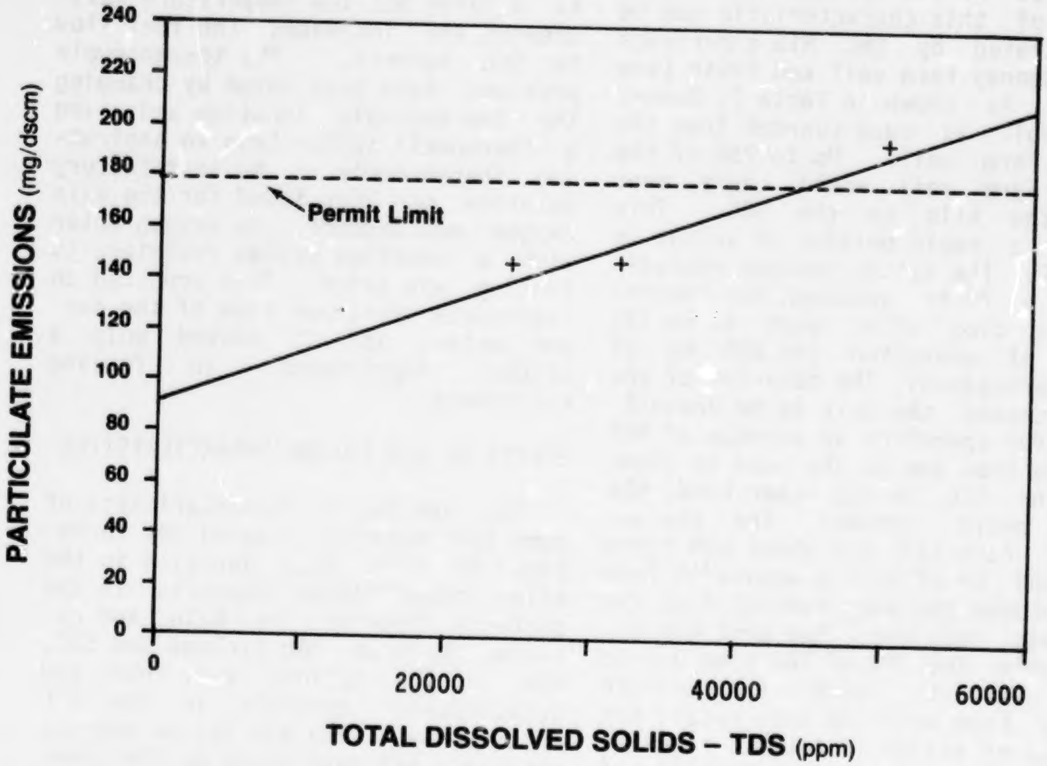
Although the cyclone has alleviated the solids buildup in the SCC, fine particulates still have caused problems with the operating instruments. The large number of fine particulates associated with brominated sludge have fouled the kiln oxygen meter and the SCC thermocouple about once every eight hours. This increases the number of over-temperature incidents in the rotary kiln, induces incinerator feed cutoff due to a false SCC low temperature measurement,and increases the fuel flow to SCC burners. The thermocouple problems have been eased by changing the thermocouple location and using a thermowell rather than an aspirating thermocouple. No satisfactory solution has been found for the kiln oxygen measurement. An oxygen meter with a sampling system resistant to fouling was tried. This produced an inadequate response time of the oxygen meter, and it showed only a slight improvement in fouling resistance.

EFFECT OF ASH FUSION CHARACTERISTICS

The ash fusion characteristics of some feed materials caused the formation of hard slag deposits in the kiln; consolidated deposits in the ductwork between the kiln and cyclone, between the cyclone and SCC, and in the cyclone exit tube; and consolidated deposits in the SCC exit venturi. The ash fusion characteristics are determined by the chemical composition of the ash.

Ashes containing elements such as sodium (Na) and potassium (K) have low slagging temperatures. Ashes from plastics, glasses, wood, and other components of trash are rich in these compounds. The increased slagging tendency of trash was experienced in the rotary kiln, which required a system shutdown about every ten days to remove the slag buildup caused by incineration of trash.

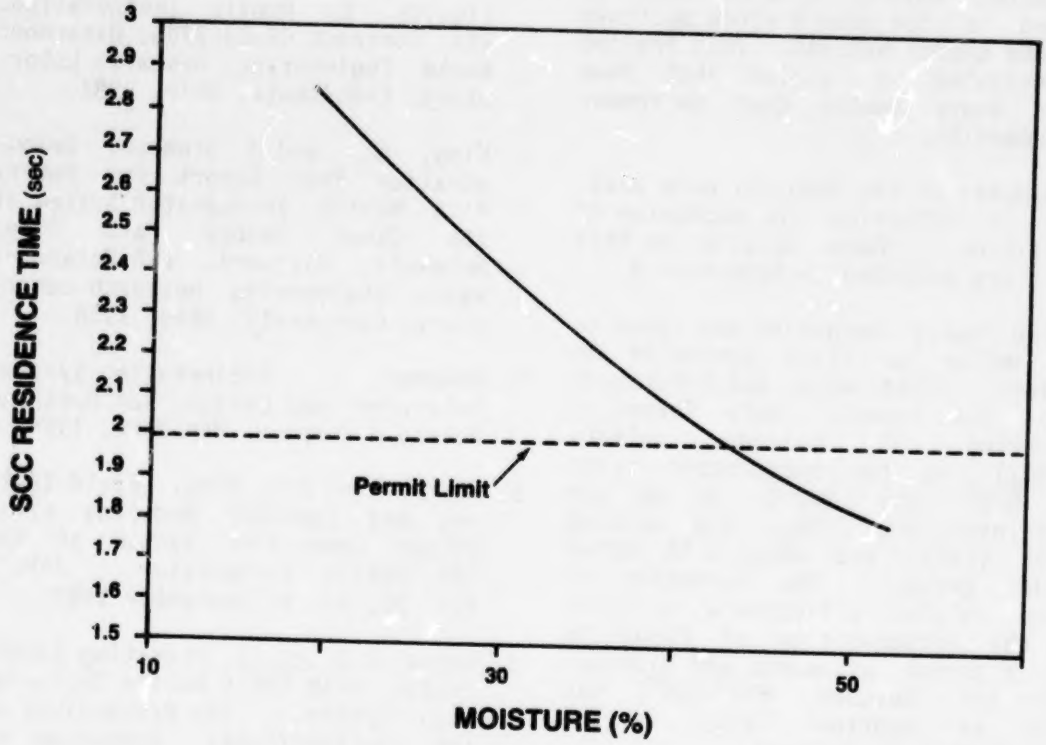
Ashes containing significant quantities of calcium (Ca), iron (Fe), sulfur (S), or phosphorous (P) have moderate slagging temperatures. Although brominated sludge, containing both Ca and S, did not slag the kiln,the ash produced a consolidated deposit, which fouled the ductwork



NOTES:

Solids Feed Rate	**1800 kg/hr**
Liquids Feed Rate	**60-160 kg/hr**
Organic Chloride Feed Rate	**50-74 kg/hr**

Figure 2. Effect of TDS on particulate emissions.



NOTES:

Solid Feed Rate	1820 kg/hr
Kiln Temperature	925°C
SCC Temperature	1200°C
30% Oxygen-Enriched Air	

Figure 3. Effect of feed moisture content on SCC residence time.

between the kiln and the SCC. A consolidated deposit also occasionally formed in the quench elbow upstream of the quench nozzles. This fouling necessitated a system shut down about every twelve days to remove the deposits.

Samples of the deposits were analyzed to determine the mechanism of deposition. More details on this topic are provided in Reference 8.

The deposit mechanism was found to be similar to those operative in boilers fired with sub-bituminous coal. The deposits were formed by sintering of calcium sulfate ($CaSO_4$) in the temperature range of 870° and 980°C in an ash containing 14% $CaSO_4$, 23% calcium oxide (CaO), and about 2.5% sodium oxide (Na_2O). The formation of fused calcium silicates as a result of the decomposition of $CaSO_4$ in the presence of quartz and aluminosilicates between 870°-980°C was also an important factor in the mechanism of deposition.

Most ashes consist mainly of aluminum (Al) and silicon (Si), which generally have good fusion characteristics (fusion temperatures above 1650°C). Both the Denney Farm and Erwin soils were composed mainly of SiO_2 and Al_2O_3. The lack of slagging and of troublesome deposits experienced with the MIS when processing these materials demonstrates these good fusion characteristics of Al and Si.

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Disclaimer

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STATE OF THE ART ASSESSMENT AND ENGINEERING EVALUATION OF MEDICAL WASTE THERMAL TREATMENT

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ABSTRACT

Incineration is a method of disposing of medical waste that is increasingly utilized to reduce the wastes volume and hazard. Recent field tests indicate that medical waste incinerators may be prone to emitting high concentrations of acid gases, toxic organic compounds and other hazardous substances. This study examined current practices in the design and operation of medical waste incinerators to identify the parameters which govern toxic emissions. A variety of design and operating parameters including chamber temperatures, gas phase mixing and waste feed rate were found to have an important impact on emissions.

INTRODUCTION

Medical waste treatment and disposal is proving to be an increasingly imposing crisis for public health. EPA estimates as much as 14,000 ton/day of medical waste are produced in hospitals in the United States (Infectious Waste News, 1988). Additional waste is produced in research and diagnostic laboratories, nursing homes, doctors offices and veterinary clinics. Not only is this waste extremely voluminous, but its infectious and sometimes radioactive nature of waste requires careful management. The technologies most commonly used to treat medical waste in the United States include steam sterilization, shredding/chemical disinfection, and incineration. Approximately 67 percent of all hospital waste is incinerated on-site. Incineration can provide up to 95 percent waste volume reduction, as well as effectively destroying infectious organisms in the waste. With landfill capacity rapidly diminishing and medical waste generation increasing, incineration is being increasingly viewed as a viable medical waste management technique.

While effective for volume/hazard reduction, incineration of medical wastes presents a unique set of problems. Destruction of hospital wastes by combustion results in formation of air pollutants in solid, liquid, condensible, and gaseous forms. This is one of the most sensitive of air pollution problems, because not only is the general public exposed to these emissions, but the greatest exposure is potentially sustained by that segment of the population which are the least capable of withstanding any further stress to their health: hospital patients.

OBJECTIVES

The ultimate goal of this research is to develop methods for controlling medical waste incinerator emissions. However, before such practices can be established, research and experimentation is required to understand the process variables that govern pollutant formation and emission from medical waste incinerators. Thus the objective of this project was to define specifically what the most critical emissions problems are and what methods are currently being used to deal with the problems.

INCINERATION SYSTEMS

There is a wide variety of medical waste incineration systems including rotary kilns, modular controlled air, and retort incinerators. Both batch fed and semi-continuous versions of all of these all these systems are used. Modular controlled air systems are by far the most commonly manufactured system in the United States at this time. In Figure 1 is shown a typical unit as designed by U.S. manufacturers. The primary zone of these systems are run fuel rich (oxygen deficient) and secondary air is usually added at the entrance to the secondary chamber to complete combustion. The waste is fed onto a small grate with pneumatic pushers that direct the burning bed through the primary chamber. The secondary chamber is normally equipped with an auxiliary fuel burner.

The principal control variables for modern controlled air incinerators are temperatures in the primary and secondary zones. Combustion air and auxiliary fuel flow are used to control the temperatures. Waste feed rate is not easily used to control primary temperature due to fact that the feed is non-continuous.

POLLUTANT FORMATION

The pollutants of concern are:

- Radioactive materials
- Pathogens
- Cytotoxic compounds
- Toxic metals
- Trace organics (e.g. PCDD/PCDF)
- Criteria pollutants (CO, NO_x, SO_2, HCl, PM, PM10)

Radioactive Materials

Radioactive materials are only a problem when present in the waste. In general, radioactive materials are segregated and disposed of separately.

Pathogens

The destruction of pathogens is one of the primary goals of medical waste incineration. There exist some data that indicate that a properly designed and operated incinerator is capable of completely destroying pathogens (Barba, 1987, Allen, 1988). These data were obtained by spiking the feed with a particular bacteria spore and then testing the residuals and exhaust gases for spore activity. Only in an incinerator operated at very low temperatures, 1100°F, was there found any residual activity.

While pathogen destruction is generally complete, an incinerator can be made to operate with poor destruction under abnormal situations. Poor carbon burnout will generally accompany pathogen emissions, i.e. the pathogens can not survive if organic carbon is destroyed. On the other hand, pathogens are likely more fragile than total organic carbon so that pathogen destruction could be accomplished without good carbon burnout. Nonetheless the factors that affect carbon burnout and pathogen destruction are related, and the parameters that control carbon burnout can be used as useful indicators of complete pathogen destruction.

The phenomena impacting carbon burnout and by analogy pathogen destruction include the following:

- waste moisture content
- uniformity of combustion zone conditions
- combustion zone temperature
- residence times of solids in the combustion zone including both solids on the bed and particles entrained into the combustion gases
- excess air levels

Cytotoxic Compounds

Dr. Nelson Slavik of the Environmental Health Management Systems representing the American Health Association recently was involved in a Workshop on Medical Waste Management. He estimates approximately 2 percent of solid waste generated by hospitals is contaminated with cytotoxic chemicals. Cytotoxic chemicals are used in chemotherapy and can themselves be both carcinogenic and mutagenic; many are listed as hazardous compounds in RCRA regulations. There are currently no standards available for the disposal of cytotoxic materials and Dr. Slavik indicated that the current disposal practices are based largely on experience.

There are no data available on the destruction efficiency of cytotoxic compounds in waste incinerators. However, since cytotoxic compounds are generally organic, organic destruction efficiency data can be used as a guide to the behavior of these materials.

Toxic Metals

Metals are present in large amounts in hospital wastes. Contaminated needles are the most obvious source of metals. However, there are a number of less obvious sources, ranging from the dyes and inks used in printed matter to some pharmaceutical preparations. It is these trace sources of metals which represent the greatest potential danger to human health, for they generally contain the most toxic metals.

In Table 1 are data from a hospital waste incinerator in California (Jenkins et al., 1987). This study indicated that the fly ash was highly enriched relative to the bottom ash with lead, cadmium, chromium and arsenic. Even when equipped with a baghouse, emission of cadmium and lead were found to be relatively high.

A number of mechanisms control the behavior of metals during the incineration of hospital wastes. These mechanisms can be identified by examining data available from a variety of incineration systems and are discussed in detail by Barton et al. (1988). The key phenomena, illustrated in Figure 2, are:

- Vaporization and subsequent condensation of volatile metals.
- Entrainment of metals bearing solids
- Reactions between metals and other elements (esp. Cl)

Some medical waste incinerators are equipped with air pollution control devices (APCDs). These units are designed to remove both gaseous compounds and solid particles from the incinerator's exhaust gases. The APCD can have a significant impact on metals emissions. The temperature at which an APCD is operated has a strong impact on the units' ability to control metals emissions. Due to their relatively low concentrations and low gas phase mobilities, metal vapors cannot be effectively captured by most APCDs. Thus the APCD must be operated at a temperature at which the metals of concern will condense.

APCD efficiency is also determined by the size distribution of the entrained particles. In general, APCDs can effectively capture large particles - those with diameters greater than 5 microns - and are less efficient at capturing small particles. Unfortunately, as discussed previously many toxic metals are concentrated on the small particles and the fume. Thus the ability of a device to capture small particles plays a key role in determining metals emissions.

The important hospital waste incinerator operating parameters that influence metals emissions can be identified using field data and an understanding of the controlling mechanisms. The most important parameter is, of course, the amount and type of metals in the waste. As previously discussed, the metals that are volatile at combustion conditions or are converted to volatile form such as As, Cd, Pb and Hg are particularly difficult to control. Other system parameters expected to influence metal emissions include the following:

- The maximum temperatures of solids in the primary zone
- Chlorine content of waste since chlorides of metals such as lead tetrachloride can form which are extremely volatile
- Primary zone gas velocity which dictates particle entrainment
- The temperature of the particle control device since this determines how much of the volatile metals have recondensed and can therefore be captured
- The fine particle control of the APCD and parameters such as pressure drop which influence the control levels.

Chlorinated Dioxin/Furans

One of the greatest challenges that remains for the disposal of medical waste by incineration is the control of emissions of trace organics such as polychlorinated dibenzo(p)dioxin and furans (PCDD/PCDF). There have now been several studies which have indicated that medical waste incinerators can generate relatively high levels of PCDD/PCDF. In Table 2 are provided data from a wide variety of combustion sources, including three medical waste incinerators that were selected to be state-of-the-art and were evaluated as part of ARB's medical waste incinerator assessment program. These data have an average total PCDD/PCDF level of approximately 700 ng/Nm^3. This is in contrast to large modern mass burn municipal waste incinerators such as Marion, Tulsa, and Wurzburg which have average total PCDD/PCDF levels of less than 30 ng/Nm^3.

The U.S. EPA is currently developing standards for the Municipal Solid Waste Incinerators to control PCDD/PCDF. Several proposed standards are being considered based upon a combination of what is achievable and the risk impacts. The current proposal would restrict new units to as low as 10 ng/Nm^3 total PCDD/PCDF (tetra- through octa-) and existing units to 125 ng/Nm^3. Hospital waste incinerators would have some difficulty in attaining these levels, based on the limited data base available to date.

Dioxins were first detected in incinerator emissions in 1977 by Ollie et al. Since that time a large number of researchers have attempted to identify the mechanisms which lead to PCDD/PCDF emissions. However no consensus has been reached.

Figure 3 illustrates the various potential mechanisms that have been proposed. One of the simplest mechanisms is that the emitted dioxins were originally present in the waste and were not destroyed in the incinerator. While this mechanism may responsible for a very small fraction of the emitted PCDD/PCDF most wastes do not contain sufficient quantities of PCDD/PCDF to account for the observed emission levels.

In the second potential mechanism, dioxins are formed as intermediates in the oxidation of more complex hydrocarbons. The hydrocarbons may be chlorinated (PVC for example) or not (cellulose). If the dioxins are originally unchlorinated the chlorination must take place as a second step.

The third potential dioxin formation mechanism involves reactions between relatively simple gas phase precursors such as phenols and chlorobenzenes. Shaub and Tsang (1983) developed a kinetic model to study the characteristics of the proposed reactions. They compared the models predictions with emissions data but were unable to determine if the proposed reactions were responsible for the dioxin emissions. Ballschmitter et al. (1983) and Benenfinati et al. (1983) examined the emissions from full scale incinerators and found a close relationship between the dioxin emissions and the quantity of polychlorobiphenol and polychlorophenol in the exhaust. They suggested that this indicates that dioxins are formed by reactions involving PCBs and PCPs. However, it is also possible that the compounds are all formed by similar sets of reactions.

The final mechanism that has been proposed calls for fly ash catalyzed formation of dioxins in relatively cool regions of the incinerator. This last mechanism was originally proposed by Vogg and Stieglitz (1983)and is supported by laboratory experiments. In the experiments, fly ash was placed in an oven and heated under controlled conditions. They found that the quantity of PCDD/PCDF increased significantly during the heating. All of the chlorine and organic precursors needed to form the dioxins were present on the particle, since none were added during the test. Extensive experiments are under way in Germany, Canada and the U.S. to extend Vogg and Stieglitz's work to full scale systems.

PCDD/PCDF emissions were found to be closely related to the quantity of entrained particles and the amount of gas phase hydrocarbons (Barton et al., 1988). Based on this analysis and other data, a mechanism for the emission of dioxins during the incineration of medical wastes can be hypothesized. The mechanism involves a series of steps. First ash particles are entrained by the gas flow. At the same time, some of the hydrocarbons present in the waste vaporize. A very small but relatively constant fraction of the hydrocarbons escape destruction in the incinerator chamber. Upon reaching a reaction zone, the hydrocarbons react on the surfaces of the particles to form dioxins. This mechanism is illustrated in Figure 4 for a hospital waste incinerator. The proposed mechanism is consistent with recent studies which indicate that the reactions occur at temperatures between 480°F and 660°F.

Based on the mechanism described above, it can be hypothesized that PCDD/PCDF formation can be minimized by controlling particle emission levels within the incinerator, minimizing the time particles are held at key temperatures (between 480°F and 666°F) and by maximizing the destruction of precursors both vapor and particle bound within the incinerator. Also dioxins can ultimately be removed from the flue gas through the use of fine particle control since PCDD/PCDF will condense on particles at low temperatures. This last approach, however, merely transfers the dioxins from one media (air) to another (ash).

Criteria Pollutants

The incineration of medical wastes can generate a variety of acid gases such as SO_2, SO_3, NO_x, HCl and HF. NO_x can be formed by oxidation of the nitrogen in air and in the wastes. The other gases are typically formed by the chemical reaction of sulfur, chlorine and other elements in the waste. The most common occurrence is the formation of HCl, and thus in most hospital waste incinerators, HCl is the principal acid gas of interest.

During combustion, the organic chloride in the waste reacts with hydrogen from the waste, auxiliary fuel, or water in the combustion chamber to form hydrogen chloride, HCl. The organic chloride can be found in many substances commonly burned in hospital waste incinerators including plastic bags, disposable syringes and plastic tubing. It is possible for free chlorine from when the combustion chamber contains an insufficient quantity of hydrogen convert all of the organic chlorine to HCl, but this is very uncommon.

Hydrogen chloride gas is highly water soluble. Thus liquid scrubbers are commonly used to control HCl emissions. The actual performance of an acid gas removal device is a complex interaction of design and operating parameters that is unique to the type of device. For these devices, three key parameters can be identified:

- Liquid to gas flow rate ratio
- pH of the feed liquid
- pH of the outlet liquid

In addition, if a venturi scrubber is used to remove HCl, the pressure drop across the scrubber is important. These parameters combined with the input levels of chlorine in hospital waste dictate the HCl emissions.

SUMMARY

The pollutants of principal concern from medical waste incinerators include:

- Volatile metals such as Ar, Pb, Cd, Hg
- Highly toxic materials such as: PCDD/PCDF and hexavalent chromium
- HCl
- Fine particles (PM10)

In certain situations radioactive materials, destruction of cytotoxic compounds and destruction of pathogens may be important issues. If radioactive materials are excluded, then the principal area of concern for both pathogen and cytotoxic compound destruction is maintaining sufficient temperature uniformly to the solids for sufficient time. The data available indicates that unusually low temperatures are required for emissions of either of these substances to be of concern.

In the case of HCl, the waste chlorine level and the performance of any air pollution control device scrubbers are dominant. Waste chlorine levels are highly variable and not easily quantified. Thus the focus comes back to the proving that the scrubber efficiency is sufficient to control any levels of HCl emissions. Since even short-term exposures to HCl are a measurable risk, the short-term control efficiency must be determined.

For toxic metals, the volatile species such as arsenic, lead and cadmium are of principal concern because they escape the incinerator as a vapor and condense into an ultrafine fume that is not easily captured and is highly respirable. However, hexavalent chromium is so toxic in small amounts that it can drive risk assessments, and therefore even small emission levels of these species are important to quantify. Again, the amount of these metals present in the hospital waste is, of course, the dominant variable for control of their emission. However, it is virtually impossible to either quantify the metals in the input waste stream or to control the levels due to the trace quantities of concern and the ubiquitous nature of many of the metals such as chromium and lead. Nonetheless this is the primary method of control and must be quantified as much as possible. For known levels of input metals, the key operating parameters are those that control the volatilization of metals (such as temperature, excess air and chlorine levels) and those that control fine particulate control.

Finally, the emissions of PCDD/PCDF are expected to be the result of a complicated interrelationship between waste properties, combustion conditions, and scrubber/fine particulate control. By analogy to MSW combustion, the primary control parameters were identified as:

- Combustion uniformity
- Combustion zone mean temperature
- Fine particle control efficiency
- APCD temperature
- Particle loading exiting furnace (determined by incinerator load, velocities and waste properties)

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METAL	INLET TO BAGHOUSE (µg/gm)	BAGHOUSE CATCH (µg/gm)	BOTTOM ASH (µg/g)
LEAD	18051	89	1700
IRON	2401	3100	17400
MANGANESE	175	240	230
NICKEL	30.7	33	33
CADMIUM	1792	1700	2.8
CHROMIUM	78	1	0.7
ARSENIC	86	4.7	0.7

TABLE 1. METAL EMISSIONS FROM CEDARS-SINAI MEDICAL CENTER INCINERATOR.

	PCDD		PCDF	
	µg/Mg	ng/Nm^3	µg/Mg	ng/Nm^3
Hospital Waste				
Cedar Sinai	1986	160-280	5384	388-700
Saint Agnes	6272	290-480	10961	700-785
Royal Jubilee	1625-2680	117-197	715-1118	52-84
Municipal Waste				
Hampton	1000-27000	243-10700	1770-41200	400-37900
North Andover		226		323
Marion Co.	5.2	.13	1.9	
Prince Edward Island	200-500	60-125	300-500	100-160
Tulsa	74.5	18.9	61.1	15.5
Wurzburg	62.7	22.1	79.2	27.9
Akron	636	258	1680	679
Tier IV				
Black Liquor		2-17		1.5-48
Wood Fired Boiler		102		154
Carbon Reg Furnace		29.8		70.1
Sewage Sludge		114		507
Drum & Barrell Reclamation		887		2107

TABLE 2. PCDD/PCDF EMISSIONS SUMMARY.

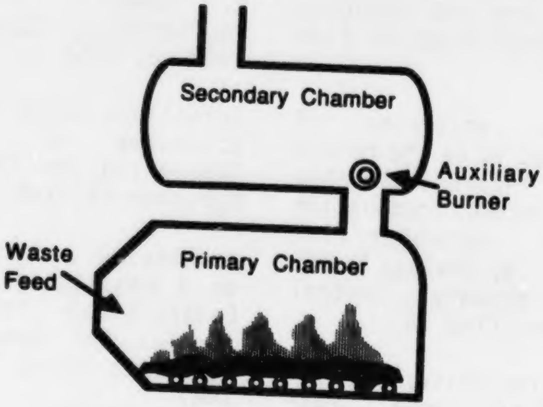

Figure 1. Typical modular starved incinerator.

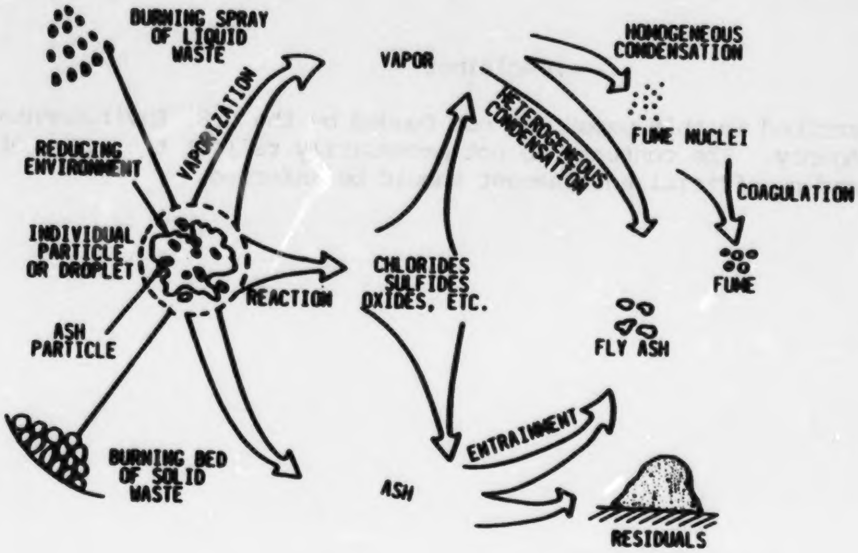
BURNING SPRAY OF LIQUID WASTE
VAPORIZATION
VAPOR
HOMOGENEOUS CONDENSATION
HETEROGENEOUS CONDENSATION
FUME NUCLEI
COAGULATION
FUME
REDUCING ENVIRONMENT
INDIVIDUAL PARTICLE OR DROPLET
REACTION
CHLORIDES SULFIDES OXIDES, ETC.
ASH PARTICLE
FLY ASH
ENTRAINMENT
BURNING BED OF SOLID WASTE
ASH
RESIDUALS

Figure 2. Phenomena affecting metals behavior during incineration.

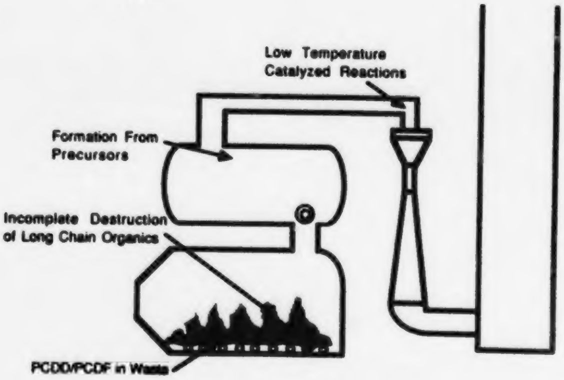
Low Temperature Catalyzed Reactions
Formation From Precursors
Incomplete Destruction of Long Chain Organics
PCDD/PCDF in Waste

Figure 3. Potential PCDD/PCDF formation mechanisms.

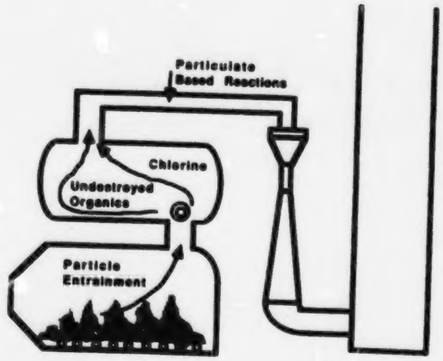
Particulate Based Reactions
Chlorine
Undestroyed Organics
Particle Entrainment

Figure 4. Hypothesized PCDD/PCDF formation mechanism.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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